2 of 2

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FINAL
OVERALL QUALITY ASSURANCE PROJECT PLAN
REMEDIAL INVESTIGATION/FEASIBILITY STUDY
FORT SHERIDAN, ILLINOIS

VOLUME 2 OF 2

Contract No. DAAA15-90-D-0017
Delivery Order 2

March 15, 1995

U.S. ARMY ENVIRONMENTAL CENTER
Aberdeen Proving Ground, MD 21010-5401

Prepared by:

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DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS IN SOLID SAMPLES BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) -(SW-846 METHOD 8270 WITH EXTRACTION METHOD 3540) USAEC METHOD SMV1

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TITLE: DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS IN SOLID SAMPLE BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (SW-846/3540/8270)
USAEC METHOD SMV1

1.0 SUMMARY AND APPLICATION

1.1 ANALYTES

This ESE standard operating procedure follows EPA SW-846 protocols with additional quality control requirements applicable for the Class 1M analysis under the USAEC guidelines for implementation of ER 1110-1-263 of the following (see Table 1.1-1) semivolatile organic compounds in extracts prepared from all types of solid waste matrices, and soils.

These compounds are classified as neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, which includes nitrophenols. This method is designed to analyze sediment and soil from hazardous waste sites for the semivolatile organic compounds including Appendix IX compounds. The method is based on SW846, Method 8270. Appendix IX compounds will only be analyzed if requested by a client.

1.2 GENERAL METHOD

Samples are prepared for analysis by SW-846 Method 3540 (Soxhlet extraction). The solid sample is mixed with anhydrous sodium sulfate, placed between two plugs of glass wool, and extracted using methylene chloride in a Soxhlet extractor. The extract is then dried through anhydrous Na_2SO_4 and concentrated. Waste samples arriving will be extracted as a solid sample. Non-aqueous (oil based) waste samples will be diluted and analyzed by direct injection.

The analysis procedure follows SW-846 Method 8270 with minor exceptions.

Deviations to the method involve using the tuning requirements and criteria from the USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Document Number OLM01.8. MS/MSD are not required for this method unless specifically requested at a particular installation. Additional USAEC QC requirements involve the analysis of two method blanks even if run times are less than 12 hours; and daily calibration response factors for two thirds of the compounds must be within a 25% difference of the average response factors for initial calibration standards (all compounds must be within a 40% difference). Table 1.2-1 presents the reporting limits and intial calibration curve levels.

1.3 INTERFERENCES

The following compounds may require special treatment when being determined by this method. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline,3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 ANALYSIS RATE

A maximum lot size of 20 environmental samples (including MS/MSD when required) is maintained for GC/MS extractions and analysis to keep analytical runs less than 24 hours.

1.5 SAFETY

Most analytes are known carcinogens. Standards, solvents, and samples must be handled carefully with proper laboratory apparel.

Table 1.1-1. GC/MS Semivolatile Target Analytes with CAS Number and USAEC Acryonym (page 1 of 2)

Analyte	CAS Registry Number	USAEC ACRONYM
BASE/NEUTRAL COMPOUNDS:		
Acenaphthene	83-32-9	ANAPNE
Acenaphthylene	208-96-8	ANAPYL
Anthracene	120-12-7	ANTRC
Benzo(a)anthracene	56-55-3	BAANTR
Benzo(b)fluoranthene	207-08-9	BBFANT
Benzo(k)fluoranthene	207-08-9	BKFANT
Benzoic acid	65-85-0	BENZOA
Benzo(g,h,i)perylene	191-24-2	BGHIPY
Benzo(a)pyrene	50-32-8	BAPYR
bis(2-Chloroethoxy)methane	111-91-1	B2CEXM
bis(2-chloroethyl)ether	111-44-4	B2CLEE
bis(2-chloroisopropyl)ether	108-60-1	B2CIPE
bis(2-ethylhexyl) phthalate	117-81-7	B2EHP
4-Bromophenyl phenyl ether	101-55-3	4BRPPE
Butylbenzylphthalate	85-68-7	BBZP
4-Chloroaniline	106-47-8	4CANIL
2-Chloronaphthalene	91-58-7	2CNAP
4-Chlorophenyl phenyl ether	7005-72-3	4CLPPE
Chrysene	218-01-9	CHRY
Dibenzo(a,h)anthracene	53-70-3	DBAHA
Dibenzofuran	132-64-9	DBZFUR
1,2-Dichlorobenzene	95-50-1	12DCLB
1,3-Dichlorobenzene	541-73-1	13DCLB
1,4-Dichlorobenzene	106-46-7	14DCLB
3,3'-Dichlorobenzidine	91-94-1	33DCBD
Diethylphthalate	84-66-2	24DCLP
Dimethylphthalate	131-11-3	DMP
Di-n-butylphthalate	84-74-2	DNBP
2,4-Dinitrotoluene	121-14-2	24DNT
2,6-Dinitrotoluene	606-20-2	26DNT
Di-n-octylphthalate	117-84-0	DNOP
Fluoranthene	106-44-0	FANT
Fluorene	86-73-7	FLRENE
Hexachlorobenzene	118-74-1	CL6BZ
Hexachlorobutadiene	87-68-3	HCBD
Hexachlorocyclopentadiene	77-47-4	CL6CP
Hexachloroethane	67-72-1	CL6ET
Indeno(1,2,3-cd)pyrene	53-70-3	ICDPYR
Isophorone	78-59-1	ISOPHR
2-Methylnaphthalene	91-57-6	2MNAP
Naphthalene	91-10-3	NAP
2-Nitroaniline	88-74-4	2NANIL
3-Nitroaniline	99-09-2	3NANIL
4-Nitroaniline	100-01-6	4NANIL
Nitrobenzene	98-59-1	NB

Table 1.1-1. GC/MS Semivolatile Target Analytes with CAS Number and USAEC Acryonym (page 2 of 2)

Analyte	CAS Registry Number	USAEC ACRONYM
N-Nitrosodi-n-propylamine	621-64-7	NNDNPA
N-Nitrosodiphenylamine	86-30-6	NNDPA
Phenanthrene	85-01-8	PHANTR
Pyrene	129-00-0	PYR
1,2,4-Trichlorobenzene	129-82-1	124TCB
ACID COMPOUNDS:		
Benzyl alcohol	100-51-6	BZALC
4-Chloro-3-methylphenol	59-50-7	4CL3C
2-Chlorophenol	95-57-8	2CLP
2,4-Dichlorophenol	120-83-2	24DCLP
2,4-Dimethylphenol	105-67-9	24DMPN
2,4-Dinitrophenol	51-28-5	24DNP
2-Methyl-4,6-dinitrophenol	534-52-51	46DN2C
2-Methylphenol	95-48-7	2MP
4-Methylphenol	106-44-5	4MP
2-Nitrophenol	88-75-5	2NP
4-Nitrophenol	100-02-7	4NP
Pentachlorophenol	87-86-5	PCP
Phenol	108-95-2	PHENOL
2,4,5-Trichlorophenol	95-95-4	245TCP
2,4,6-Trichlorophenol	88-06-2	246TCP

Table 1.2-1. Reporting Limits, and Upper and Lower Initial Calibration Standard Range for Semivolatile Organic Compounds in Soil - USAEC SW-846 Method 8270 (page 1 of 2).

Parameter	Reporting Limit* (µg/g)	Lower Std. (µg/mL)	Upper Std. (µg/mL)
Phenol	0.14	2.0	160
bis(2-Chloroethyl) ether	0.14	2.0	160
2-Chlorophenol	0.14	2.0	160
1,3-Dichlorobenzene	0.14	2.0	160
1,4-Dichlorobenzene	0.14	2.0	160
1,2-Dichlorobenzene	0.14	2.0	160
2-Methylphenol	0.14	2.0	160
2,2'-oxybis(1-chloropropane)	0.14	2.0	160
4-Methylphenol	0.14	2.0	160
N-Nitroso-di-n-propylamine	0.14	2.0	160
Hexachloroethane	0.14	2.0	160
Nitrobenzene	0.14	2.0	160
Isophorone	0.14	2.0	160
2-Nitrophenol	0.14	2.0	160
2,4-Dimethylphenol	0.14	2.0	160
Benzoic acid	1.35	20	160
bis(2-Chloroethoxy)methane	0.14	2.0	160
2,4-Dichlorophenol	0.14	2.0	160
1,2,4-Trichlorobenzene	0.14	2.0	160
Naphthalene	0.14	2.0	160
4-Chloroaniline	0.30	2.0	160
Hexachlorobutadiene	0.14	2.0	160
4-Chloro-3-methylphenol	0.14	2.0	160
2-Methylnaphthalene	0.14	2.0	160
Hexachlorocyclopentadiene	1.0	10	160
2,4,6-Trichlorophenol	0.30	2.0	160
2,4,5-Trichlorophenol	0.30	2.0	160
2-Chloronaphthalene	0.14	2.0	160
2-Nitrolaniline	0.67	10	160
Dimethylphthalate	0.14	2.0	160
Acenaphthylene	0.14	2.0	160
2,6-Dinitrotoluene	0.14	2.0	160
3-Nitroaniline	0.67	10	160
Acenaphthene	0.14	2.0	160
2,4-Dinitrophenol	1.35	20	160
4-Nitrophenol	1.35	20	160
Dibenzofuran	0.14	2.0	160
2,4-Dinitrotoluene	0.14	2.0	160
Diethylphthalate	0.14	2.0	160
4-Chlorophenyl-phenylether	0.14	2.0	160
Fluorene	0.14	2.0	160
4-Nitroaniline	0.67	10	160

Table 1.2-1. Reporting Limits, and Upper and Lower Initial Calibration Standard Range for Semivolatile Organic Compounds in Soil - USAEC SW-846 Method 8270 (page 2 of 2).

	Parameter	Reporting Limit* (μg/g)	Lower Std. (μg/mL)	Upper Std. (μg/mL)
	4,6-Dinitro-2-methylphenol	1.35	20	160
	N-nitrosodiphenylamine	0.14	2.0	160
	4-Bromophenly-phenylether	0.14	2.0	160
	Hexachlorobenzene	0.14	2.0	160
	Pentachlorophenol	0.67	10	160
	Phenanthrene	0.14	2.0	160
	Anthracene	0.14	2.0	160
	Carbazole	0.14	2.0	160
	Di-n-butylphthalate	0.14	2.0	160
	Fluoranthene	0.14	2.0	160
	Pyrene	0.14	2.0	160
	Butylbenzylphthalate	0.14	2.0	160
	3,3'-Dichlorobenzidine	0.67	10	160
	Benzo(a)anthracene	0.14	2.0	160
	Chrysene	0.14	2.0	160
	bis(2-Ethylhexyl)phthalate	0.14	2.0	160
	Di-n-octylphthalate	0.14	2.0	160
	Benzo(b)fluoranthene	0.14	2.0	160
	Benzo(k)fluoranthene	0.14	2.0	160
	Benzo(a)pyrene	0.14	2.0	160
	Indeno(1,2,3-cd)pyrene	0.16	2.0	160
	dibenzo(a,h)anthracene	0.16	2.0	160
	Benzo(g,h,i)perylene	0.16	2.0	160
**	Thiophenol	NA		
**	Tris-2,3-dibromopropyl phospate	NA		
**	Dimethoate	NA		
**	Isopropyl Alcohol	NA		
**	1,4-Naphthoquinone	NA		

* Based on ESE's MDL studies; however the reporting limits of compounds that are difficult to analyze were adjusted to a concentration that is detected more reliably. The MDL studies were conducted according to the 40 CFR 136 Appendix B protocols. MDLs are required annually to support the chosen reporting limits.

+ To convert the upper and lower initial calibration concentrations to soil units of ug/g divide by 15 g (2 ug/mL coverts to 0.13 ug/g).

NA These analytes are requested for some projects and will be reported as TIC (see section 5.3)

** These compounds will be determined by automated library search. If found, a RRF of 1.0 will be used for quantitation.

2.0 APPARATUS AND CHEMICALS

2.1 INSTRUMENTATION

2.1.1 Gas Chromatograph--An analytical system complete with a temperature programmable gas chromatograph suitable for splitless injection of all required accessories including syringes, analytical columns, and gases.

2.1.2 Column--30 m x 0.25 mm ID (or 0.32 mm) bonded-phase silicone coated fused silica capillary column (J&W Scientific DB-5 or equivalent). A film thickness of 0.25 micron may be used.

2.1.3 Mass Spectrometer--Capable of scanning from 35 to 500 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all required criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

2.1.4 Data System--A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

2.1.5 The following sytstems are currently available for SVOAs:

			Injector Temp.	Transfer Line Temp.
1.	HP-1000/RTE-6V/M Computer			
	a.	HP-5985 GC/MS	280°C	290°C
	b.	HP-5988 GC/MS	290°C	295°C
2.	HP-1000/RTE-A Computer (A400)			
	a.	HP5970B GC/MS	280°C	315°C
	b.	HP5970B GC/MS	280°C	315°C
3.	HP-3000 Computer HP-UX (425T)			
	a.	HP-5972A GC/MS	250°C	300°C
4.	Finnigan INCOS DG10 Computer			

a.	INCOS 50 GC/MS	280°C	250°C

2.1.6 GC/FID equipped with same column for screening purposes.

2.2 GLASSWARE AND HARDWARE

2.2.1 Soxhlet extractor: 40-mm I.D., with 500-mL round-bottom flask.

2.2.2 Long Stem funnel: 75 mm top diameter (Kimax 2895075 or equivalent).

2.2.3 Kuderna-Danish (K-D) apparatus:

2.2.3.1 Concentrator tube: graduated ground glass stopper is used to prevent evaporation of extracts.
2.2.3.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.
2.2.3.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).
2.2.3.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

2.2.4 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

2.2.5 Vials: Glass autosampler, with Teflon lined crimp cap.

2.2.6 Glass wool: Contaminant free.

2.2.7 Heating mantle: Rheostat controlled.

2.2.8 Syringe: 5-mL., 10μL

2.2.9 Apparatus for grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. A ceramic mortar and pestle will be used to process samples to meet this criteria. This procedure should handle most solid samples, except gummy, fibrous, or oily materials.

2.3 REAGENTS AND STANDARDS

2.3.1 Sodium sulfate: (ACS) Granular anhydrous (purified by washing with methylene chloride followed by heating at 400°C for 4 hr in a shallow tray).

2.3.2 Extraction solvent: Methylene chloride - pesticide quality or equivalent.

2.3.3 Internal Standards--1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}. Commercially produced internal standard solution from Protocol Analytical supplier P-CLPS-12 @ 2000 ug/mL. Spike 20 uL to achieve 40 ng/uL.

2.3.4 Calibration standards -- Supelco (or other acceptable vendor) standard mixes (see section 3.1.1 for preparation). Prepare calibration standards at a minimum of seven concentration levels. Each calibration standard should contain each compound of interest and each surrogate standard. Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10°C to -20°C in screw-cap amber bottles with Teflon liners. Fresh standards should be prepared every 12 months or sooner if comparison with a quality control check sample indicates a problem.

2.3.5 Surrogate Solutions -- Commercially produced Protocol (or other acceptable vendor) stock solutions (2000 ug/mL of acids and 1000 ug/mL of bases) of CLP/SW-846 acid surrogates (2FP, PHEND6, and 246TBP) and base/neutral surrogates (NBD5, 2FBP, and TRPD14). Five mL of each solution are added to a 100 mL volumetric flask and brought to volume with methanol. The resulting solution has a concentration of 50 ug/mL for base/neutrals and 100 ug/mL for acids. One mL of this spiking solution is added to each 15 g soil sample. The resulting target concentration in ug/g is 3.33 for base/neutrals and 6.67 ug/g for acids.

2.3.6 Matrix Spike Solutions -- Commercially produced Protocol (or other acceptable vendor) matrix spike stock solutions (2000 ug/mL of acids and 1000 ug/mL of bases) of CLP/SW-846 acid compounds (PHENOL,

PCP, 4NP, 2CLP, and 4CL3C) and base/neutral surrogates (ANAPNE, 14DCLB, 24DNT, NNDNPA and 124TCB). Five mL of each solution are added to a 100 mL volumetric flask and brought to volume with methanol. The resulting solution has a concentration of 50 ug/mL for base/neutrals and 100 ug/mL for acids. One mL of this spiking solution is added to each 15 g soil sample. The resulting target concentration in ug/g is 3.33 for base/neutrals and 6.67 ug/g for acids.

2.3.7 USAEC Standard Soil for the method blank.

2.3.8 Reagent water: Reagent water is defined as water in which an interferant is not observed at the method detection limit of the compounds of interest.

3.0 CALIBRATION

3.1 INITIAL CALIBRATION

Initial calibration occurs when an instrument is first set up or after major maintenance and when the daily calibration curve (performed every 12 hours) does not meet criteria. Response factors for each compound are calculated for each standard and a relative response factor (RRF) and relative standard deviation (RSD) are calculated across the initial calibration range. A maximum RSD of $\leq$ 30% is allowed for each compound flagged as a calibration check compound (CCC) (see Section 3.1.2.1). Preparation of initial calibration standards is described below. The analysis of the calibration standards is performed as defined in Section 5.2 following proper tuning defined in Section 7.1.

3.1.1 Preparation of Calibration Standards

3.1.1.1 Combined Working Solutions

Prepare a 200 ug/mL combined working standard (CWS) by combining 2 mL of the following standard mixes (4.0 mL for B/N surrogates mix) to a 20 mL volumetric flask:

Supelco TCL Base Neutral Mix 1	2000 ug/mL in $MeCl_2$
Supelco TCL Base Neutral Mix 2	2000 ug/mL in $MeCl_2$
Supelco TCL PAH Mix	2000 ug/mL in $MeCl_2$/Benzene 50:50
Supelco TCL Phenols Mix	2000 ug/mL in $MeCl_2$
Supelco TCL Benzidines Mix	2000 ug/mL in Methanol
Supelco TCL Hazardous Substance-Mix 1	2000 ug/mL in $MeCl_2$
Supelco TCL Hazardous Substance-Mix 2	2000 ug/mL in $MeCl_2$
Protocol CLP Acid Surrogate Mix	2000 ug/mL in Methanol
Protocol CLP Base Neutral Surr. Mix	1000 ug/mL in $MeCl_2$/Acetone

3.1.1.2 Calibration Standards

Calibration standards are prepared following the dilutions listed below:

Standard:	Combine:
10 ug/mL	50 uL of 200 ug/mL CWS + 950uL $MeCl_2$
20 ug/mL	100 uL of 200 ug/mL CWS + 900uL $MeCl_2$
50 ug/mL	250 uL of 200 ug/mL CWS + 750uL $MeCl_2$

80ug/mL	400 uL of 200 ug/mL CWS + 600uL $MeCl_2$
120ug/mL	600 uL of 200 ug/mL CWS + 400uL $MeCl_2$
160ug/mL	800 uL of 200 ug/mL CWS + 200uL $MeCl_2$
2 ug/mL	100 uL of 20 ug/mL calibration standard + 900uL $MeCl_2$

3.1.2 Analyze each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. Calculate relative response factors (RRF) for each compound using equation 1.

$$\text{Eq 1:} \quad RRF = \frac{(A_x C_{is})}{(A_{is} C_x)}$$

where:
A_x = Area of the characteristic ion for the compound to be measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the internal standard (ng/uL).
C_x = Concentration of the compound to be measured (ng/uL).

3.1.2.1 Calculate an average RRF and relative standard deviation (RSD) for all compounds for the calibration standards . A system performance check must be made before this calibration curve is used. Four compounds (the system performance check compounds) are checked for a minimum average relative response factor of 0.05. These compounds (the SPCC) are N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol. The response factors over the initial calibration curve concentrations will have less than or equal to 30-percent RSD for the calibration check compounds (CCC) listed below or the initial calibration must be repeated (Note: pentachlorophenol will be calibrated from 10 ug/mL to 160 ug/mL):

Calibration Check Compounds	m/z
Phenol	94
1,4-Dichlorobenzene	146
2,4-Dichlorophenol	162
Hexachlorobutadiene	225
4-Chloro-3-methylphenol	107
2,4,6-Trichlorophenol	196
Acenaphthene	154
Fluoranthene	202

Benzo(a)pyrene	252
2-Nitrophenol	139
N-Nitrosodiphenylamine	169
Pentachlorophenol	266
Di-n-octylphthalate	149

3.2 DAILY CALIBRATION

A check of the calibration curve must be performed once every 12 hours during analysis. One mL of the 50 ug/mL standard is used for daily calibration (see Section 3.1.1 for preparation). The minimum relative response factor for the system performance check compounds must be checked and greater than or equal to 0.05. If this criteria is met, the relative response factors of all compounds are calculated. A percent difference of the daily (12 hour) relative response factor compared to the average relative response factor from the initial curve is calculated. The % difference for two thirds of all compounds must be $\leq$ 25%. In addition all compounds must be within $\pm$ 40% of the average RRF from initial calibration. If this criteria is not met, reanalyze the daily standard. If the daily standard fails again, perform a new initial curve.

4.0 SAMPLE HANDLING AND STORAGE

Soil samples must be extracted within 7 days of sample collection and extracts must be analyzed within 40 days of sample extraction. Samples are collected and shipped to the laboratory at 4 degrees C in either 250 or 500 mL wide mouth glass amber jars. Samples are stored at the laboratory at 4 degrees C until extraction.

4.1 SOLUTION VERIFICATION

Surrogate solutions are verified with each run (the extraction group provides a sample of the surrogate solution for analysis if the surrogates in the samples and method blank show problems). Calibration solutions are monitored by analysis of the daily calibration standard and its comparison to the initial calibration curve.

5.0 EXTRACTION AND ANALYSIS PROCEDURE

5.1 EXTRACTION PROCEDURE

Samples requiring analysis (determined from sample arrival notices) are checked out of the cold room for extraction. Check the arrival notice to determine whether MS/MSDs are required for this project (if required, spike the required volume indicated on the bottle to the required sample, see section 5.1.3, preparation defined in section 7.4). Two method blanks of USAEC standard soil are required for each lot. Determination of percent moisture: Sample results are desired based on a dry-weight basis. A portion of the sample will be used for moisture determination (note this is a separate analysis at ESE and not performed by the extractor). Proceed as follows:

5.1.1 Do not decant any water from the sample. However, if excessive water is present, consult with the Supervisor. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

5.1.2 Place sufficient glass wool in the bottom of the Soxhlet extractor to cover the drain hole. Place 300 mL of methylene chloride into a 500 mL flat-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor, place condenser in the extractor (be sure water is flowing through the condenser) and extract the wool for at least one hour. Turn extractor off, allow to cool and discard the methylene chloride.

5.1.3 Blend 15 g of the solid sample with enough anhydrous sodium sulfate to dry the sample. It should have a sandy texture. Place in precleaned Soxhlet. If Method 3640, Gel-permeation cleanup, is to be used (see ESE SOP's in Attachment 1), add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column. (Note: GPC may be necessary for a project after the first set of samples is analyzed and it is determined that GPC will be required due to sample matrix.) Add the required volume (indicated on the bottle) of the Surrogate Standard Spiking Solution onto the sample. For the sample in each analytical batch selected for spiking, add the required volume (indicated on the bottle) of the appropriate matrix spiking standard, **if requested**.

5.1.4 Place 300 mL methylene chloride into the precleaned 500-mL flat-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hr.

5.1.5 Allow the extract to cool after the extraction is complete.

5.1.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 25 mL concentrator tube to a 500-mL evaporation flask.

5.1.7 Dry the extract by passing through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect dried extract in the K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of methylene choride to complete the quantitative transfer.

5.1.8 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (60 -70°C which is above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 min. When the apparent volume of liquid reaches 10 mL remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

5.1.9 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride.

5.1.10 Add a clean boiling chip to the concentrator tube and attach a modified micro Snyder. Prewet the column by adding 0.5 mL of CH_2Cl_2 to the top of the column. Place the concentrator tube in a hot water (60-70°C). When the apparent volume of liquid reaches 0.5 mL,remove from the water bath and allow to cool and drain for at least 10 min.

5.1.11 Remove micro-Snyder and quantitatively tranfer the extract to a graduated autosampler vial, adjusting the final volume to 1.0 mL with CH_2Cl_2. Label properly. The extract is now ready for GC/MS analysis.

When extraction is complete make a copy of all pertinent extraction notebooks, summary forms and extract chain of custody. Transfer labeled extracts to appropriate coldroom for storage at 4 degrees C prior to analysis. When GPC is required ESE has 2 SOPs for different equipment: SOP-ASG3242-001 and SOP-ASG3242-002 (Att. 1).

5.2 ANALYSIS PROCEDURES

Prior to GC/MS analysis, physical characterization or an optional GC/FID screen of extracts can be performed. Physical characterization involves the visual evaluation of the extract, e.g. viscosity is a good indicator of high concentrations of oils. Additional GC/FID screen may be performed. The GC/FID screen injects a 50 ng/uL phenanthrene standard for comparison to the sample extract. The undiluted sample extract is analyzed on the GC/MS when no peaks, other than the surrogates, are detected, or when other peaks are detected but the response is less than the surrogates or the 50 ng/uL phenanthrene standard. Appropriate dilutions are performed on the sample extract when any peaks are greater than the 50 ng/uL phenanthrene standard. Dilutions for the GC/MS analysis are determined by the dilution required from GC/FID screening to reduce the major peaks to between one-half and full response of the 50 ng/uL phenanthrene standard.

5.2.1 Each GC/MS system must have the hardware tuned to meet the criteria listed in section 7.1.3 for a 50 ng injection of decafluorotriphenyl phosphine (DFTPP). No sample analyses can begin until all these criteria are met. The following instrumental parameters are required for all performance tests and for all sample analyses:

Electron Energy:	70 volts (nominal)
Mass Range:	35 to 500 amu
Scan Time:	not to exceed 1 second per scan

5.2.2 Twenty uL of the 2,000 ng/uL internal standard solution (section 2.3.3) is added to each 1.0 mL sample extract, standard, or blank. The internal standards selected should permit most components of interest in a chromatogram to have relative retention times of 0.80 to 1.20 relative to the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation. If interferences are noted, use the next most intense ion as the secondary ion. The internal standards are:

1,4-Dichlorobenzene-d_4	152 m/z
Naphthalene-d_8	136 m/z
Acenaphthene-d_{10}	164 m/z
Phenanthrene-d_{10}	188 m/z
Chrysene-d_{12}	240 m/z
Perylene-d_{12}	264 m/z

5.2.3 Analyze the 1.0 mL extract by GC/MS using a bonded-phase silicone-coated fused silica capillary column. The recommended GC operating conditions to be used are as follows (note actual injector temperatures and tranasfer line temperature are defined for each instrument in section 2.1.5):

Initial Column Temperature Hold:	40°C for 4 minutes
Column Temperature Program:	40°C-280°C at 10 degrees/min.
Final Column Temperature Hold:	280°C for 10 min.
Injector Temperature:	250°C-300°C
Transfer Line Temperature:	250°C-315°C
Source Temperature:	200°C
Injector-Grob-type, splitless	
Sample Volume:	1 - 2 uL
Carrier Gas:	Helium

5.2.4 Make any extract dilution indicated by screening characterization prior to the addition of internal standards. If any further dilutions of water or soil/sediment extracts are made, additional internal standards must be added to maintain the required 40 ng/uL of each constituent in the extract volume. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons.

5.2.5 Compounds shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra. Table 5.2-1 presents the quantitation ion used for each compound.

5.2.5.1 For establishing correspondence of the GC RRT, the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. Comparison of standard and sample component mass spectra obtained on ESE GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the GC/MS

meets the DFTPP daily tuning requirements. These standard spectra may be obtained from the run used to obtain reference RRTs.

5.2.5.2 The requirements for qualitative verification by comparison of mass spectra are as follows:
A)All ions present in the standard mass spectra at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.
B)The relative intensities of ions specified in the preceding paragraph must agree within plus or minute 20 percent between the standard and sample spectra. (Example: For an ion with an abundance of 50 percent in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)
C)Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra.

5.2.5.3 If a compound cannot be verified by all of the criteria in Section 5.2.5, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then report that identification and proceed with quantitation in Section 6.

5.2.6 Internal standard responses and retention times in all samples should be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system should be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards should be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system should be inspected for

malfunction and corrections made as appropriate. If the analysis of a subsequent sample or standard indicates that the system is functioning properly, then corrections may not be required. The samples or standards with EICP areas outside the limits should be re-analyzed. If corrections are made, then the laboratory must demonstrate that the mass spectrometric system is functioning properly. This must be accomplished by the analysis of a standard or sample that does meet the EICP criteria. Sample re-analysis required when system was malfunctioning.

Table 5.2-1. GC/MS Target Analytes, Internal Standards and Quantitation Ions (page 1 of 2).

Analyte	Quantitation Ion	Internal* Standard
Acenaphthene	153	3
Acenaphthylene	152	3
Anthracene	178	4
Benzo(a)anthracene	228	5
Benzo(b)fluoranthene	252	6
Benzo(k)fluoranthene	252	6
Benzoic acid	122	2
Benzo(ghi)perylene	276	6
Benzo(a)pyrene	252	6
Benzyl alcohol	108	1
bis(2-chloroethoxy)methane	93	2
bis(2-chloroethyl) ether	93	1
bis(2-chloroisopropyl) ether	45	1
bis(2-ethylhexyl) phthalate	149	5
4-Bromophenyl phenyl ether	248	4
Butylbenzyl phthalate	149	5
4-Chloroaniline	127	2
4-Chloro-3-methylphenol	107	2
2-Chloronaphthalene	162	3
2-Chlorophenol	128	1
4-Chlorophenyl phenyl ether	204	3
Chrysene	228	5
Dibenzo(a,h)anthracene	278	6
Dibenzofuran	168	3
1,2-Dichlorobenzene	146	1
1,3-Dichlorobenzene	146	1
1,4-Dichlorobenzene	146	1
3,3'-Dichlorobenzidine	252	5
2,4-Dichlorophenol	162	2
Diethyl phthalate	149	3
2,4-Dimethylphenol	107	2
Dimethyl phthalate	163	3
Di-n-butyl phthalate	149	4
2,4-Dinitrophenol	184	3
2,4-Dinitrotoluene	165	3
2,6-Dinitrotoluene	165	3
Di-n-Octyl phthalate	149	6
Fluoranthene	202	4
Fluorene	166	3
Hexachlorobenzene	284	4
Hexachlorobutadiene	225	2
Hexachlorocyclopentadiene	237	3
Hexachloroethane	117	1
Indeno(123-cd)pyrene	276	6
Isophorone	82	2

Table 5.2-1. GC/MS Target Analytes, Internal Standards and Quantitation Ions (page 2 of 2).

Analyte	Quantitation Ion	Internal* Standard
2-Methyl-4,6-dinitrophenol	198	4
2-Methylnaphthalene	142	2
2-Methylphenol	108	1
4-Methylphenol	108	1
Naphthalene	128	2
2-Nitroaniline	65	3
3-Nitroaniline	138	3
4-Nitroaniline	138	3
Nitrobenzene	77	2
2-Nitrophenol	139	2
4-Nitrophenol	109	3
N-Nitrosodi-n-propylamine	70	1
N-Nitrosodiphenylamine	169	4
Pentachlorophenol	266	4
Phenanthrene	178	4
Phenol	94	1
Pyrene	202	5
1,2,4-Trichlorobenzene	180	2
2,4,5-Trichlorophenol	196	3
2,4,6-Trichlorophenol	196	3

* LEGEND FOR INTERNAL STANDARD

Code	Internal Standard	Quantitation Ion
1	1,4-Dichlorobenzene-D(4)	152
2	Naphthalene-D(8)	136
3	Acenaphthene-D(10)	164
4	Phenanthrene-D(10)	188
5	Chrysene-D(12)	240
6	Perylene-D(12)	264

5.3 TENTATIVELY IDENTIFIED COMPOUND SEARCH

A library search shall be executed for sample components for the purposes of tentative identification. For this purposes, the 1989 release of the WILEY/NIST Library containing 130,000 spectra (or the 1990 release of the NIST/EPA/MSDC Library containing 54,000 spectra), shall be used. Most ESE instrumentation and computers have the 1990 version but the instrument in Section 2.1.5.4 has the 1986 release.

5.3.1 All nonsurrogate organic compounds with responses greater than 10 percent of the nearest internal standard and not listed for the combined base/neutral/acid fraction shall be tentatively identified via a forward search of the Wiley/NIST mass spectral library. (Substances with responses less than 10 percent of the nearest internal standard are not required to be searched in this fashion.) Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

NOTE: Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

5.3.2 Guidelines for Making Tentative Identification

5.3.2.1 Relative intensities of major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum.

5.3.2.2 The relative intensities of the major ions should agree within $\pm 20\%$. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.

5.3.2.3 Molecular ions present in reference spectrum should be present in sample spectrum.

5.3.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

5.3.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting compounds. NOTE: Data system library reduction programs can sometimes create these discrepancies.

5.3.3 If in the technical judgement of the mass interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

6.0 CALCULATIONS

6.1 Components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte.

6.2 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a relative response factor is calculated using the secondary ion.

6.2.1 Calculate the concentration in the sample using the relative response factor (RRF) as determined in Section 3.1.2 and the following equation:

$$\text{Concentration, } \mu g/g = \frac{(A_x)(I_s)}{(A_{is})(RRF)(W_s)(D)}$$

A_x = Area of the characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the internal standard
I_s = Amount of internal standard added to the extract in micrograms (ug)
W_s = Weight of sample extracted (grams)
$D = \frac{100\text{-\% moisture}}{100}$

6.3 An estimated concentration for components tentatively identified shall be quantified by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

6.3.1 The formula for calculating concentrations is the same as in the previous paragraph.

6.3.2 Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

6.4 Calculate surrogate standard recovery on all sample, blanks, and spikes. Determine if recovery is within limits and report.

6.5 ESE's QA/QC manual lists the accuracy, precision, and reporting limit data for the semivolatiles compounds that were validated using this method.

7.0 DAILY QUALITY CONTROL

7.1 TUNING

7.1.1 Each GC/MS system must have the hardware tuned to meet the criteria listed for a 50 ng injection of decafluorotriphenyl phosphine (DFTPP). No sample analyses can begin until all these criteria are met. This criteria must be demonstrated each 12 hour shift. DFTPP has to be injected to meet this criterion. Post-acquisition manipulation of abundances is not acceptable.

7.1.2 DFTPP Key Ion Abundance Criteria

7.1.2.1 Prior to the analysis of any samples, blanks, or calibration standards, the GC/MS must establish that the system meets the mass spectral ion abundance criteria for the instrument performance check solution containing decafluorotriphenylphosphine (DFTPP).

7.1.2.2 The analysis of the instrument performance check solution may be performed as an injection of up to 50 ng of DFTPP into the GC/MS.

7.1.3 The analysis of the instrument performance check solution must meet the ion abundance criteria given below:

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA FOR QUADRAPOLE MASS SPECTROMETERS

Mass	Ion Abundance Criteria
51	30.0 - 80.0 percent of mass 198
68	Less than 2.0 percent of mass 69
69	Present
70	Less than 2.0 percent of mass 69
127	25.0 - 75.0 percent of mass 198
197	Less than 1.0 percent of mass 198
198	Base peak, 100 percent relative abundance (see note)
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	Greater than 0.75 percent of mass 198
441	Present but less than mass 443
442	40.0 - 110.0 percent of mass 198
443	15.0 - 24.0 percent of mass 442

NOTE: All ion abundances MUST be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110 percent that of m/z 198.

7.1.4 The abundance criteria listed above must be met for a 50 ng injection of DFTPP. The mass spectrum of DFTPP must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan prior to the elution of DFTPP. Note: All subsequent standards, samples, and blanks associated with a DFTPP analysis must use identical mass spectrometer instrument conditions.

7.1.5 The instrument performance check solution must be analyzed once at the beginning of each 12-hour period during which samples or standards are analyzed. The twelve (12) hour time period for a GC/MS system instrument performance check and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as an instrument performance check. The time period ends after twelve (12) hours has elapsed according to the system clock.

Reference: USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Document Number OLM01.8.

7.2 METHOD BLANK

7.2.1 Method blanks (using the USAEC standard soil) must be analyzed for each 12 hours of sample run.

7.2.2 Two method blanks will be supplied with each batch of samples. If the analytical sample run is less than 12 hours, both method blanks must be analyzed.

7.3 CONTINUING CALIBRATION CHECK

7.3.1 The 50 μg/mL standard will be analyzed at the beginning of a sample sequence, after DFTPP has passed criteria, and before any samples or blanks.

7.3.2 The RRFs for all compounds must be calculated and two thirds of them must be ≤25% different from the average RRF determined from the seven point initial calibration. In addition, all compounds must be ≤ 40% different from the average RRF.

7.4 SAMPLES

7.4.1 All samples and blanks will be spiked with surrogates.

7.4.2 Surrogate recoveries will be calculated for each sample and blank.

7.4.2.1 If recoveries of two surrogate compounds, i.e. - 2 acids or 2 BN are outside established limits, the extract must be reanalyzed. Failure of one acid and/or 1 BN does not initiate reanalysis. If reanalysis solves the problem, only report the reanalysis. If the extract still fails upon reanalysis document that reanalysis was performed and that surrogate recovery is matrix dependent.

7.4.2.2 Recovery ranges for the surrogates are:

COMPOUND	PERCENT RECOVERY
Nitrobenzene-d_5	23-120
2-Fluorobiphenyl	30-115
p-terphenyl-d_{14}	18-137
Phenol-d_5	24-113
2-Fluorophenol	25-121
2,4,6-Tribromophenol	19-122

7.4.3 As an optional project specific quality control parameter, calculate matrix spike/matrix spike duplicate (MS/MSD) recoveries. MS/MSD should be performed on 5% of a batch, or 1 MS/MSD per 20 samples from the same project, when requested. The recovery ranges are based on SW846, 3rd edition guidelines. The MS/MSD compounds are:

Compound	Recovery Range*	MSD-RPD*
Phenol	26-90%	35 %
2-Chlorophenol	25-102%	50 %
1,4-Dichlorobenzene	28-104%	27 %
N-Nitroso-di-n-propylamine	41-126%	38 %
1,2,4-Trichlorobenzene	38-107%	23 %

4-Chloro-3-methylphenol	26-103%	33 %
Acenaphthene	31-137%	19 %
4-Nitrophenol	11-114%	50 %
2,4-Dinitrotoluene	28-89%	47 %
Pentachlorophenol	17-109%	47 %
Pyrene	35-142%	36 %

* These ranges are advisory ranges only. Failure to achieve this will not initiate reanalysis.

7.5 CONTROL CHARTS

Control charts shall be maintained for surrogate control analytes spiked in the method blank. Control charts are used to monitor the variations in the precision and accuracy of routine analyses and detect trends in these variations. Data from the laboratory analyses will be used to initially construct control charts. Data used in control charts shall not be adjusted for accuracy. Data from spiked QC samples within a lot will be compared to control chart limits to demonstrate that analyses of the lot are under control and the in control data will be used to update the charts. Control charts are prepared for all of the surrogate analytes using the percent recovery data calculated according to the following equation:

$$\textit{Percent Recovery} = \frac{\textit{Found Concentration}}{\textit{Spiked Concentration}} \; x \; 100$$

Preparation of control charts requires the following data: An average percent recovery (X) of the surrogate in the two spiked QC samples (method blanks) in the analytical lot; and a percent difference for the percent recovery of the surrogate in the two spiked QC samples (method blanks) in the analytical lot.

8.0 REFERENCE

8.1 ESE SOP-ASM3241-002, Gas Chromatography/Mass Spectrometry (GC/MS) Determination of Semivolatile Organics (EPA 8270 and Appendix IX Compounds), Rev.

8.2 EPA Method 8270 - Test Methods for Evaluating Solid Wastes, EPA SW 846, 3rd Edition, September 1986.

8.3 USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Document Number OLM01.8.

8.4 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

9.0 ATTACHMENTS

Attachment 1: ESE SOP-ASG3242-001 and SOP-ASG3242-002 for GPC cleanup.

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) - SW-846 8240
PACKED COLUMN METHOD - USAEC VMS-1
CAPILLARY COLUMN METHOD - USAEC VMS-2

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DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) - SW-846 8240 PACKED COLUMN METHOD - USAEC VMS-1 CAPILLARY COLUMN METHOD - USAEC VMS-2

1.0 SUMMARY AND APPLICATION

1.1 SUMMARY

This Standard Operating Procedure (SOP) follows EPA SW-846 protocols with additional quality control requirements applicable for the CLASS 1M analysis as specified in the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993). USEPA Contract Laboratory Program (CLP) Statement of Work for Organic Analysis, Document Number ILM01.8 allows for the analysis of VOA's by either packed or capillary columns. USAEC has required the assignment of two separate method numbers for the two columns but has agreed to the interchangeable use of either method since reporting limits have been designed to be consistent for both columns and method detection limits studies for each column support the reporting limits. Analytical capacity is the major reason for allowing the interchangeable use of either method. Data in the USAEC data base and control charts will distinguish between which method was used.

GC/MS tuning procedure and criteria follows guidelines as specified in OLM01.8. Additional QC requirements include analysis of two method blanks if the run is less than 12 hours and two thirds of the compounds must be within a 25% difference of the average RRF from daily calibration, all compounds must be within a 40% difference.

The method includes an optional hexadecane screening procedure. The extract is screened on a gas chromatograph/flame ionization detector (GC/FID) to determine the approximate concentration of organic constituents in the sample. For analysis an inert gas is bubbled through a 5 mL sample contained in a specifically designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph (GC) is temperature programmed to separate the purgeables which are then detected with a mass spectrometer (MS).

1.2 APPLICATION

This SOP is applicable to the determination of volatile organic compounds in water matrix by Gas Chromatography/Mass Spectrometry (GC/MS). Volatile (VOA) analysis of water samples must be completed within 14 days of sampling date. The analytical method that follows is designed to analyze water, from hazardous waste sites for the organic VOA compounds and Appendix IX compounds. The following compounds will be analyzed.

ANALYTE	ACRONYM	CAS Number
Acetone	ACET	67-64-1
Benzene	C6H6	71-43-2
Bromodichloromethane	BRDCLM	75-27-4
Bromoform	CH3BR	75-25-2
Bromomethane	ETHBR	74-83-9
2 - Butanone	MEK	78-93-3
Carbon Disulfide	CS2	75-15-0
Carbon Tetrachloride	CCL4	56-23-5
Chlorobenzene	CLC6H5	108-90-7
Chloroethane	C2H5CL	75-00-3
2-Chloroethyl Vinyl Ether	2CLEVE	110-75-8
Chlorform	CHCL3	67-66-3
Chloromethane	CH3CL	74-87-3
Dibromochloromethane	DBRCLM	124-48-1
1,1 - Dichloroethane	11DCLE	75-34-3
1,2 - Dichloroethane	12DCLE	107-06-2
1,2 - Dichloroethene, total	12DCE	540-59-0
1,1 - Dichloroethene	11DCE	75-35-4
1,2 - Dichloropropane	12DCLP	78-87-5
cis - 1,3 - Dichloropropene	C13DCP	10061-01-5
trans - 1,3 - Dichloropropene	T13DCP	10061-02-6
Ethylbenzene	ETC6H5	100-41-4
2 - Hexanone	MNBK	591-78-6
4 - Methyl - 2 - pentanone	MIBK	108-10-1
Methylene Chloride	CH2CL2	75-09-2
Styrene	STYR	100-42-5
1,1,2,2 - Tetrachloroethane	TCLEA	79-34-5
Tetrachloroethene	TCLEE	127-18-4
1,1,1 - Trichloroethane	111TCE	71-55-6
1,1,2 -Trichloroethane	112TCE	79-00-5
Trichloroethene	TRCLE	79-01-6
Toluene	MEC6H5	108-88-3
Vinyl Acetate	C2AVE	108-05-4
Vinyl Chloride	C2H3CL	75-01-4
Xylene, total	TXYLEN	-
1-Chloro-2,3-epoxypropene	——	-
Acetonitrile	CH3CN	-
Ethylene oxide	ETOX	-
Methyl methacrylate	PLEXI	-

1.3 REPORTING LIMITS AND INITIAL CALIBRATION RANGES

Table 1.3-1 defines the reporting limits for the analytes analytes and the upper and lower initial calibration curve ranges. MDL studies are performed annually on both columns to confirm the validity of the chosen reporting limits following the procedure of 40 CFR Volume 4 No. 136, Appendix B.

1.4 INTERFERENCES

Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and the solvent vapors in the laboratory account for the majority of the contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and shipment. A trip blank is prepared from reagent water and carried through the sampling and handling protocol to serve as a check on such contamination. Contamination by carryover can occur whenever high level and low level samples are sequentally analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

The laboratory where volatile analysis is performed should be completely free of solvents.

1.5 ANALYSIS RATE

Ten samples can be analyzed in an 8 hour shift.

1.6 SAFETY INFORMATION

Each compound should be treated as a potential health hazard. Inhalation of vapors, especially from neat volatile compounds should be avoided.

Table 1.3-1. Reporting Limits, and Upper and Lower Standard Range for Volatile Organic Compounds in Water, Method 5030/8240

Parameter	Reporting Limit (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)
Acetone	10	10	200
Benzene	2	2	200
Bromodichloromethane	2	2	200
Bromoform	2	2	200
Bromomethane	2	2	200
2 - Butanone	10	10	200
Carbon Disulfide	10	10	200
Carbon Tetrachloride	2	2	200
Chlorobenzene	2	2	200
Chloroethane	10	10	200
2-Chloroethyl Vinyl Ether	10	10	200
Chlorform	2	2	200
Chloromethane	2	2	200
Dibromochloromethane	2	2	200
1,1 - Dichloroethane	2	2	200
1,2 - Dichloroethane	2	2	200
1,2 - Dichloroethene, total	2	2	200
1,1 - Dichloroethene	2	2	200
1,2 - Dichloropropane	2	2	200
cis - 1,3 - Dichloropropene	2	2	200
trans - 1,3 - Dichloropropene	2	2	200
Ethylbenzene	2	2	200
2 - Hexanone	10	10	200
4 - Methyl - 2 - pentanone	10	10	200
Methylene Chloride	10	10	200
Styrene	2	2	200
1,1,2,2 - Tetrachloroethane	2	2	200
Tetrachloroethene	2	2	200
1,1,1 - Trichloroethane	2	2	200
1,1,2 -Trichloroethane	2	2	200
Trichloroethene	2	2	200
Toluene	2	2	200
Vinyl Acetate	10	10	200
Vinyl Chloride	2	2	200
Xylene, total	10	10	200
1-Chloro-2,3-epoxypropene	NA		
Acetonitrile	NA		
Ethylene oxide	NA		
Methyl methacrylate	NA		

NA = Information not available. A library search can be performed for the qualitative evaluation of samples for these compounds. No reporting limits have been established.

2.0 APPARATUS AND CHEMICALS

2.1 HARDWARE/GLASSWARE

2.1.1 Micro syringes: 10 uL and larger, 0.006 inch ID needle.

2.1.2 Disposable micropipettes: Various 5, 10, 20, 25, 100, 250 uL.

2.1.3 Syringe valve: Two-way, with Luer ends (three each), if applicable to the purging device.

2.1.4 Syringe: 5 mL, gas tight with shut-off valve.

2.1.5 Balance: Analytical, capable of accurately weighing $\pm$0.0001 g and a top-loading balance capable of weighing $\pm$0.1 g.

2.1.6 Glassware:

2.1.6.1 Bottle: 40 mL or 60 mL, screw cap, with Teflon cap liner.
2.1.6.2 Volumetric flasks: Class A with ground-glass stoppers.
2.1.6.3 Vials: 2 mL for GC autosampler.

2.1.7 Purge and trap device: The purge and trap device consists of three separate pieces of equipment; the sample purger, trap, and the desorber. Several complete devices are commercially available. This SOP was developed using Tekmar LSC 2000 concentrator interfaced to a Tekmar 2016 sixteen position autosampler <u>or</u> a Tekmar LSC 4000 concentrator interfaced to a Tekmar ALS ten position autosampler.

2.1.7.1 The sample purger must be designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger must meet the design criteria specified in the method. Alternate sample purge devices may be utilized provided equivalent performance is demonstrated.

2.1.7.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed to contain the following minimum lenghts of absorbents: 15 cm 2,6-diphenylene oxide polymer (Tenax-GC, 60/80 mesh) and 8 cm of silica gel (Davidson Chemical, 35/60 mesh, grade 15, or equivalent) and 1 cm 3% SP-2100, Supelco Catalog #2-0293.

2.1.7.3 The desorber should be capable of rapidly heating the trap to 220°C. The polymer section of the trap should not be heated higher than 220°C, and the remaining sections should not exceed 220°C during bakeout mode. The desorber design must meet these criteria.

2.1.7.4 The purge and trap device is coupled to a GC.

2.2 INSTRUMENTATION (GC/MS SYSTEM)

2.2.1 GC: An analytical system complete with a temperature programmable GC suitable for on-column injection and all required accessories including syringes, analytical columns, and gases.

2.2.2 Packed Column: 6 ft long x 0.1 in. ID glass, packed with 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent. Note: Capillary columns may be used for the analysis of volatile compounds by this method if the internal standards and surrogate compounds specified in this SOP are utilized and demonstrates the performance and QA/QC criteria contained in this SOP.

Capillary Column: 30Mx0.53 mm, ID with Jet Seperator, 75Mx0.53 mm ID capillary direct.

2.2.3 MS: Capable of scanning from 35 to 260 amu every 3 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria. One uL (50 ng) of 4-bromoflurobenzene (BFB) is injected through the GC inlet on the instruments identified in section 2.2.6.1 and 2.2.6.2. Alternately, 50 ng of BFB is purged as an introduction method to determine instrument tuning compliance on instruments identified in section 2.2.6.3 and 2.2.6.4.

2.2.4 GC/MS: Any GC to MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the parameters of interest and achieves all acceptable performance criteria may be used. GC to MS interfaces are constructed of all glass or glass-lined materials. Glass can be deactivated by silanizing with dichlorodimethylsilane.

2.2.5 Data System: A computer must be interfaced to the MS that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

2.2.6 The following systems are currently available for volatile compound analyses (instruments are equiped with capillary columns unless identified for packed):

1. HP-1000/RTE-6V/M Computer
   a. HP-5985 GC/MS (packed column)
   b. HP-5996 GC/MS (packed column)

2. HP-1000/RTE-A Computer (A400)
   a. HP5970B GC/MS

3. HP-3000 Computer HP-UX (425T)
   a. HP-5989 Engine

4. Finnigan INCOS MV-1000 Computer
   a. INCOS XLe

2.3 REAGENTS AND STANDARDS

2.3.1 Reagents:

2.3.1.1 Reagent Water: Reagent water is defined as water in which an interference is not observed at or above the EPA CRQLs of the parameters of interest. (Methylene Chloride, Acetone, Toluene and 2-Butanone $\leq$ 5 xCRQL). Reagent water is prepared by

using double steam distilled water purged at 70°C with UPC grade helium overnight, and is held at constant temperature while purging continuously.

2.3.1.2 Methanol: Purge and trap grade.

2.3.2 Standards

2.3.2.1 Stock Standards:

2.3.2.1.1 Commercially prepared standards are used at the concentration certified by the manufacturer.

2.3.2.1.2 Store at -10°C to -20°C and protect from light.

2.3.2.1.3 Once a stock solution is opened it may be used at most one week.

2.3.2.1.4 All standards should be replaced after six months or sooner if comparison with check standards indicates a problem (e.g., degradation, concentration).

2.3.2.1.5 Use Supelco prepared standard mixtures or other acceptable vendor. Table 2.3-1 in Attachment A identifies the compounds in each of the following mixtures:

1. Supelco Purgeable A: 4-8851 200 ug/mL
2. Supelco Purgeable B: 4-8852 200 ug/mL
3. Supelco Purgeable C: 4-8853 200 ug/mL
4. Protocol HSL Cat# P-CLPV-D 1000 ug/mL

2.3.2.1.6 Purgeables Internal Standard Mix: CLP Supelco 4-8835 or equivalent at 1000 ug each component in 1 mL of methanol. The three internal standards are bromochloromethane, chlorobenzene-d_5, and 1,4-difluorobenzene.

2.3.2.2 Working Standard Solutions:

Combine 200 uL of each A,B,C stocks at 200 ug/mL solution and 200 uL of dilute HSL (at 200 ug/ml) to make 800 uL of a 50 ug/mL solution. Make four more working standard solutions combining in the same manner and label as Notebook No.:, Page No.:, Entry No.: A,B,C,D, and E. Store in

freezer between -10°C and -20°C and use each aliquot as needed (e.g., 441-85-2A, 441-085-2B, 441-85-2C). One mL of Protocol HSL(P-CLPV-D) at 1000 ug/mL is added to a 5 mL volumetric flask and diluted to mark to yeild a 200 ug/mL solution.

Standards must be stored in sealed vials at -10°C to -20°C and protected from light. If not so stored, they must be discarded after an hour.

2.3.2.3 Surrogate Standard Spiking Solution:

Supelco Purgeables Surrogate Standard Mix - CLP 4-8876 at 250 ug/mL each in methanol: bromofluorobenzene, 1,2-dichloroethane-d_4, and toluene-d_8 for waters. 200 uL of CLP 4-8876 surrogate mix is added to 800 uL of MeOH in a wheaton vial to yeild a 50 ug/mL solution.

2.3.2.4 Purgeable Organic Matrix Standard Spiking Solution/QC Reference (**PROJECT SPECIFIC, when requested**). For sample matrix spikes, **when requested**, a 5 uL aliquot of the Supelco CLP volatile matrix spiking solution (Catalog No. 4-8399) is added to two portions from one sample chosen for spiking (each compound is 50 ug/L). Compounds are benzene, chlorobenzene, toluene, trichloroethylene, and 1,1-dichloroethylene.

2.3.2.5 Internal Standards Daily Spiking Solution

Dilute 500 uL of Stock Internal Standard Solution (Section 2.3.2.1.6) at 1,000 ug/mL to 10.0 mL with methanol to yield a 50 ug/mL daily spiking solution. Record in standards log and label.

2.3.2.6 Purchased neat BFB is purchased from Aldrich or an other acceptable vendor (density 1593 ug/uL). Prepare 20,000 ug/mL primary stock solution by adding 125 uL of neat BFB to methanol in a 10 mL volumetric and bring to mark. Prepare 50 ug/mL working solution by adding 25 uL of the primary stock to methanol in a 10 mL volumetric and bring to mark.

Transfer to five or six ~2 mL sealed crimp top vials and store between -10°C and -20°C. Use each aliquot as needed. The primary is good for two years and the working solutions are good for six months.

2.3.2.7 Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10°C to -20°C in crimp-top bottles with Teflon liners and record and label as routine.

3.0 CALIBRATION

3.1 INITIAL CALIBRATION

Initial calibration occurs when a check of the daily calibration curve (performed every 12 hours) does not meet criteria. A percent difference of the daily (12 hour) relative response factor compared to the average relative response factor from the initial curve is calculated. A maximum percent difference of $\leq$ 25% is allowed for each compound flagged as "CCC" (see section 3.1.2.2 for stability/performance verification compounds). Preparation of initial calibration standards is described below. The analysis of the calibration standards performed as defined in Section 5.2 Analysis procedure.

3.1.1 Preparation of Initial Calibration Standards

Section 2.3.2.2 defines how to prepare the 50 ug/mL working standard solution. The following standards are prepared by adding the required volume of the working standard solution to 5 mL of standard water in the purge tube:

Std. Conc. ug/L	Volume of Stock uL
200	20
100	10
50	5
20	2
10	1
2	2*

* The 2 ug/L standard is prepared by using a 1:10 dilution of the working standard solution.

3.1.2 Analyze each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. The response factors for each compound are calculated from the area counts for the primary ion of the target compounds compared to the area of the primary ion of the appropriate internal standard. Table 5.1-1 presents the primary and secondary ions for identification and the associated intenal standard for each

compound. Calculate relative response factors (RRF) for each compound using equation 1.

$$\text{Eq 1:} \qquad RRF = \frac{(A_x C_{is})}{(A_{is} C_x)}$$

where:
A_x = Area of the characteristic ion for the compound to be measured.
A_{is} = Area of the characteristic ion for the specific internal standard.
C_{is} = Concentration of the internal standard (ng/uL).
C_x = Concentration of the compound to be measured (ng/uL).

3.1.2.1 Calculate an average RRF and relative standard deviation (RSD) for all compounds for the calibration standards . A system performance check must be made before this calibration curve is used. Five compounds [(the system performance check compounds (SPCC)] are checked for a minimum average RRF. These compounds (the SPCC) are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. RRFs must be $\geq$0.30, except bromoform $\geq$0.25. The response factors over the certified range will have less than 30-percent RSD for the calibration check compounds (CCC). If the RSD of the average RRF of any of the CCCs is greater than 30 percent, the initial calibration must be repeated. The CCC compounds are:

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl Chloride

3.2 DAILY CALIBRATION

The 50 ug/L standard (5 uL of the 50 ug/mL working stock) is used for daily calibration (see Section 3.1.1 for preparation). The analysis of the calibration standards performed as defined in Section 5.0 following tuning procedures defined in Section 7.1. Use Equation 1, Section 3.1.2 to calculate RRF's for each compound. The percent difference of the daily RRF compared to the average RRF from the initial curve must be $\leq$ 25% for two thirds of the

compounds (including CCC's). All compounds must be within $\pm$ 40% except ketones, methylene chloride and chloroethane. If this criteria is not met, reanalyze the daily standard. If the daily standard fails again - perform a new initial six point curve.

3.2.1 A check of the calibration curve must be performed once every 12 hours during analysis. The minimum relative response factor for the system performance check compounds must be checked. If this criteria is met, the relative response factors of all compounds are calculated. A percent difference of the daily (12 hour) relative response factor compared to the average relative response factor from the initial curve is calculated. A maximum percent difference of $\leq$ 25% is allowed for each compound flagged as "CCC". Only after both these criteria are met can sample analysis begin.

3.2.2 Internal standard responses and retention times in all standards should be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system should be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards should be monitored and evaluated for each standard. If EICP area for any internal standard changes by more than a factor of two (-50 percent to +100 percent), the mass spectrometric system should be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning may be necessary.

4.0 SAMPLE HANDLING AND STORAGE

4.1 Samples (60-mL volume) will be collected using adequate dermal and inhalation protection and must follow Sections 3.3 and 3.4 of the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

4.2 Sample containers consist of 40-mL amber-colored bottles with Teflon-lined septa. The sample bottles must be prepared according to Appendix C of the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

4.3 Samples should be kept chilled to 4°C and in the dark.

4.4 The holding time limit for completion of analysis is 14 days from the sampling date. (Unpreserved samples have a holding time limit of 7 days.)

4.5 Verification of the calibration standards is based on the daily calibration control criteria, analysis of independent reference standards when available, and comparison of mass spectra with reference spectra from the Wiley/NIST database. If the 25 percent difference criteria cannot be met for the stability/performance check compounds, a new standard solution must be analyzed.

4.6 The verification of the surrogate spiking solution is based on control chart criteria. If more than one of the three surrogate analytes are designated out-of-control, a new surrogate spiking solution must be prepared.

5.0 PROCEDURE

Assemble a purge and trap device that meets the specification in Section 2.1.7. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 cm^3/min or in an oven. Daily, prior to use, condition the traps for 10 minutes while backflushing at 180°C with the column at 220°C. Connect the purge and trap device to a GC. The GC must be operated using temperature and flow rate parameters equivalent to those in Section 5.2. Tune the GC/MS system according to Section 7.1 by analyzing 50 ng of bromofluorobenzene (BFB) to meet the criteria listed in Section 7.1.4. Daily calibration of the purge and trap-GC/MS system is performed using internal standards (Section 3.2). Analyze samples as discussed below following optional screening Section 5.16. Table 5.1-1 summarizes the primary and secondary quantitation ions and the appropriate internal standard for each compound. Section 6.1 discusses compound identification. Section 6.2 discusses calculations for final concentrations for the identified compounds. Section 6.3 discusses tentatively identified compound searches.

5.1 GC/MS Operating conditions:

These performance test required the following instrumental parameters:

Electron Energy:	70 Volts (nominal)
Mass Range:	35 - 300 amu
Scan Time:	To give at least 5 scans per peak and not to exceed 3 seconds per scan.

5.2 Analytical procedure for water sample analysis:

5.2.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

5.2.2 Operating conditions for the GC packed column instruments (Section 2.2.6.1.a and b): Carbopak B (60/80 mesh) with 1 percent SP-1000 packed in a 1.8 m by 2 mm ID glass column to a jet separator with helium carrier gas at a flow rate of 30 cm^3/min. Column temperature is isothermal at 35°C for 3 minutes and then programmed @ 8°C/min to 225°C (220°C for instrument 2.2.6.1.b) and held for 15 minutes. Injector temperature is 200-225°C. Source temperature is set according to the manufacturer's specifications. Transfer line temperature is 230°C.

Operating conditions for the GC capillary column instruments (Section 2.2.5.2.a, 3.a and 4.a): Instrument 2.2.5.2.a is set up with a 30 m DB624 capillary column to a jet separator. The initial temperature is 10°C held for 5 minutes then programmed to 135°C at 7.5°C/min. Instrument 2.2.5.3.a is set up with a 75 m DB624 capillary column direct to MS. The initial temperature is 35°C held for 4 minutes then programmed to 175°C at 8.0°C/min. Instrument 2.2.5.4.a is set up with a 105 m (Restec 502.4) 0.53 mm ID capillary column to a jet separator. The initial temperature is 45°C held for 3.2 minutes then programmed to 160°C at 6.7°C/min then programmed to 210°C at 13.3°C/min. Injector temperatures are 200-225°C. Source temperature is set according to the manufacturer's specifications. Transfer line temperatures are 230°C.

5.3 After achieving the key ion abundance criteria for BFB, calibrate the system daily.

5.4 Adjust the purge gas (helium) flow rate to 25-40 cm^3/min. Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

5.5 Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample or standard bottle which has the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the sample for future analysis so if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such a time when the analyst has determined that the first sample has been analyzed properly. Filling one 20 mL syringe would allow the use of only one syringe. If a second analysis is needed from the 20 mL syringe, it must be analyzed within 24 hours. Care must also be taken to prevent air from leaking into the syringe.

5.6 The purgeable organics screening procedure, if used, will have shown the approximate concentrations of major sample components. If a dilution of the sample was indicated, this dilution shall be made just

prior to GC/MS analysis of the sample. All steps in the dilution procedure must be performed without delays until the point at which the diluted sample is in a gas-tight syringe.

5.6.1 The following procedure will allow for dilutions near the calculated dilution factor from the screening procedure: fill the 5 mL syringe with Organic Free Water (OFW). If a 1:5 dilution is required, displace 1 mL of OFW from the syringe to leave 4 mL of OFW. Using Research helium displace a 1 mL aliquot into the syringe with the OFW and make to 5 mL.

5.7 Add 5 uL of the surrogate spiking solution (Section 2.3.2.3) and 5 uL of the internal standard spiking solution (Section 2.3.2.5) through the valve bore of the syringe, then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 5 uL of the surrogate spiking solution to a 5 mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

5.8 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

5.9 Close both valves and purge the sample for 11.0 $\pm$ 0.1 minutes at ambient temperature.

5.10 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the GC temperature program. Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 220^{0}C while backflushing the trap with an inert gas between 20 and 60 cm^3/min for four minutes.

5.11 While the trap is being desorbed into the GC, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water to avoid carryover of pollutant compounds.

5.12 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. The trap temperature should be maintained at 180^{0}C. Trap temperatures up to 220^{0}C may be employed, however the higher temperature will shorten

the useful life of the trap. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample. Alternative trap is baked out @ 260°C.

5.13 If the initial analysis of a sample or a dilution of a sample has concentration of compounds that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. NOTE: For total xylenes, where three isomers are quantitated as two peaks, the calibration range of each peak should be considered separately (e.g., a diluted analysis is not required for total xylenes unless the concentration of either peak separately exceeds 200 ug/L). Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is used, document the reasons. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

5.14 For water samples, add 5 uL of the matrix spike solution prepared at 50ng/uL (Section 2.3.2.4) to the 5 mL of sample purged. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.

5.15 All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

5.16 Optional VOA GC/FID screen - Remove 2 mL of sample from the ~40 mL sample vial. Add 2 mL of hexadecane to the vial. Place on a wrist action shaker for twenty minutes. Remove from wrist action shaker and remove the hexadecane layer, i.e. the top layer and place in a crimp top autosampler vial. Screen by GC/FID.

5.16.1 Prepare a standard by spiking 5 uL of a 25 mg/mL standard solution containing benzene, chlorobenzene, 1,1 dichloroethene, toluene, and trichloroethene into 40 mL of reagent water in a VOA bottle. Add 2 mL of hexadecane and

extract as described in Section 5.16 (Concentration = 62.5 ng/uL).

5.16.2 GC/FID Screen - Inject 3 uL of the 62.5 ng/uL VOA standard described in 5.16.1. Inject the sample screen extract and compare the response of the peaks to the standard response. The sample will be analyzed neat by GC/MS when no peaks are detected or any peaks are less than one-half the peak responses of the standard. Appropriate dilutions for GC/MS analysis is performed when any peaks are greater than one-half of the peak responses of the standard.

Table 5.1-1. **Quantitation Ions and Internal Standards.**

Analyte	Primary Ion	Secondary Ion(s)	Internal* Standard
Acetone	43	58	A
Benzene	78	–	B
Bromodichloromethane	83	85	B
Bromomethane	94	96	A
2-Butanone	72	57	A
Carbon disulfide	76	78	A
Bromoform	173	171,175,250	B
Carbon Tetrachloride	117	119,121	B
Chlorobenzene	112	114	C
Chloromethane	50	52	A
2-Chloroethylvinyl ether	106	63,65	B
Chloroform	83	85	A
Chloroethane	64	66	A
Dibromochloromethane	129	208,206	B
1,1-Dichloroethane	63	65,83,85	A
1,2-Dichloroethane	62	64,100,98	A
1,1-Dichloroethene	96	61,98	A
1,2-Dichloroethene	96	61,98	A
1,2-Dichloropropane	63	65,114	B
cis-1,3-Dichloropropene	75	77	B
trans-1,3-Dichloropropene	75	77	B
Ethylbenzene	106	91	C
2-Hexanone	43	58,57,100	C
Methylene Chloride	84	48,51,86	A
4-methyl-2-Pentanone	43	58,100	C
Styrene	104	78,103	C
1,1,2,2-Tetrachloroethane	83	83,131,135,166	C
Tetrachloroethene	164	129,131,166	C
Toluene	92	91	C
1,1,1-Trichloroethane	97	99,117,119	B
1,1,2-Trichloroethane	97	83,85,99,132,134	B
Trichloroethene	130	95,97,132	B
Trichlorofluoromethane	101	103	A
Vinyl acetate	43	86	B
Vinyl chloride	62	64	A
o-Xylene	106	91	C
m-Xylene	106	91	C
p-Xylene	106	91	C
4-Bromofluorobenzene	95	174,176	C
1,2-Dichloroethane-D(4)	65	102	A
Toluene-D(8)	98	70,100	C
Internal Standards:			
Bromochloromethane	128	49,130,51	A
1,4-Difluorobenzene	114	63,88	B
Chlorobenzene	117	82,119	C

6.0 IDENTIFICATION, QUANTITATION, AND TENTATIVE IDENTIFICATIONS

6.1 COMPOUND IDENTIFICATION

6.1.1 The compounds shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compounds. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time (RRT) as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

6.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within $\pm$ 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

6.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the GC/MS meets the daily tuning requirements for BFB. These standard spectra may be obtained from the run used to obtain reference RRTs.

6.1.1.4 The requirements for qualitative verification by comparison of mass spectra are as follows:

6.1.1.4.1 All ions present in the standard mass spectra at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.

6.1.1.4.2 The relative intensities of ions specified in Section 3.11 must agree within $\pm$ 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50 % in the standard spectra, the corresponding sample abundance must be between 30 and 70 %).

Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be

considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra.

6.1.1.5 If a compound cannot be verified by all of the criteria in Section 6.1.2.2, but in the technical judgement of the mass spectral interpretation specialist, the identification is correct, then report that identification and proceed with quantitation in Section 6.2.

6.2 Quantitative Determinations

6.2.1 Components identified shall be quantitated by the internal standard method. The internal standard used shall be that which is listed. The EICP area of the characteristic ions of analytes listed are used.

6.2.2 Internal standard responses and retention times in all standards should be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system should be inspected for malfunctions, and corrections made as required. The EICP of the internal standards should be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50 to +100 %), the MS system should be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning may be necessary.

6.2.3 The RRF from the daily standard analysis is used to calculate the concentration in the sample. Use the RRF as determined in section 3.5 and the equations below.

$$\text{Concentration ug/L} = \frac{(A_x)(I_s)}{(A_{is})(RRF)(V_o)}$$

A_x = area of the characteristic ion for the compound to be measured,
A_{is} =area of the characteristic ion for the specific internal standard,
I_s = amount of internal standard added in nanograms (ng), and
V_o= volume of water purged in mL (account for dilutions).

6.2.4 An estimated concentration for components tentatively identified shall be quantitated by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

6.2.4.1 The formula for calculating concentrations is the same as in Section 6.2.3. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A RRF of one is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

6.2.5 Xylenes (o-, m-, and p- isomers) are to be reported as Xylenes (total). Since o- and p-Xylene overlap, the Xylenes must be quantitated as m-Xylene. The concentration of all Xylene isomers must be added together to give the total.

6.2.6 1,2-Dichloroethene (trans and cis steroisomers) are to be reported as 1,2-Dichloroethene (total). The concentrations of both isomers must be added together to give the total, especially for the capillary column method option where isomers are resolved.

6.2.7 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits and report.

6.2.7.1 Calculation for surrogate recovery:

$$\% \ Surrogate \ Recovery = \frac{Q_d}{Q_a} \ x \ 100\%$$

where: Q_d = quantity determined by analysis, and
Q_a = quantity added to sample.

6.2.7.2 If recovery is not within limits, the following is required:

6.2.7.2.1 Check to be sure there are no errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance.

6.2.7.2.2 Reanalyze the sample if none of the above reveal a problem.

6.2.7.3 If the reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only report data from the analysis with surrogate spike recoveries within the limits. This is considered the initial analysis and shall be reported as such on all data deliverables, however all runs are included on run logs and identified as why the run was not used. All runs will be included in data package.

6.2.7.4 If the reanalysis of the sample does not solve the problem (i.e., surrogate recoveries are outside the limits for both analysis), then check the surrogates in the method blank and spike check. If the surrogates in the method blank and spike check are within limits, qualify the data.

6.2.7.5 If the sample with surrogate recoveries outside the limits is the sample used for the matrix spike and matrix spike duplicate, and the surrogate recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), then the sample, matrix spike, and matrix spike duplicate do not require reanalysis. Document the similarity in surrogate recoveries.

6.2.7.6 ESE's QA Manual lists the accuracy, precision and reporting limit data of the Appendix IX organic volatile compounds that were validated using this method.

6.3 TENTATIVELY IDENTIFIED COMPOUND SEARCH

6.3.1 A library search shall be executed for sample components for the purpose of tentative identification. For this purpose, the 1989 release of the NIST Mass Spectral Library (or more recent release), containing 130,000 spectra, shall be used. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

6.3.2 All nonsurrogate non target organic compounds with responses greater than 10 percent of the internal standard shall be tentatively identified via a forward search of the Wiley/NIST mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

6.3.3 Guidelines for making tentative identification are as follows:

6.3.3.1 Relative intensities of major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum).

6.3.3.2 The relative intensities of the major ions should agree within ± 20 percent. (Example: For an ion with an abundance of 50 % of the standard spectra, the corresponding sample ion abundance must be between 30 and 70 %).

6.3.3.3 Molecular ions present in reference spectrum should be present in sample spectrum.

6.3.3.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

6.3.3.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

6.3.4 If in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

7.0 DAILY QUALITY CONTROL

7.1 TUNING

7.1.1 Prior to the analyses of any samples, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing p-bromofluorobenzene (BFB).

7.1.2 The analysis of the instrument performance check solution is performed as follows:

7.1.2.1 A 1 uL injection of the working BFB solution (Section 2.3.2.6) (50 ng of BFB) into the GC/MS for instruments listed in 2.2.6.1 and 2.2.6.2.

7.1.2.2 Add 1 uL of the working BFB solution (Section 2.3.2.6) (50 ng of BFB) to 5.0 mL of reagent water and analyzing the resulting solution as if it were an environmental sample (see sample analysis procedure) on instruments 2.2.6.3 and 2.2.6.4.

7.1.2.3 BFB may not be analyzed simultaneously with a calibration standard.

7.1.3 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan prior to the elution of BFB.

NOTE: All subsequent standards, samples, MS/MSD, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

7.1.4 The analysis of the instrument performance check solution must meet the ion abundance criteria given below.

BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	8.0 - 40.0 percent of mass 95
75	30.0 - 66.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of mass 95 (see note)
173	less than 2.0 percent of mass 174
174	50.0 - 120.0 percent of mass 95
175	4.0 - 9.0 percent of mass 174
176	93.0 - 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

NOTE: All ion abundances must be normalized to m/z 95, the nominal base peak, even through the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

7.1.5 The instrument performance check solution must be injected once at the beginning of each 12-hour period, during which samples or standards are to be analyzed. The twelve (12) hour time period for GC/MS Instrument Performance Check (BFB), standards calibration (initial or continuing calibration criteria) and method blank analysis begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. The time period ends after twelve (12) hours has elapsed according to the system clock.

Ref. USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Document Number ILM01.8.

7.2 METHOD BLANK

7.2.1 Method blanks must be analyzed for each 12 hours of sample run.

7.2.2 Two method blanks will be supplied with each batch of samples. If the analytical sample run is less than 12 hours, both method blanks must be analyzed.

7.3 CONTINUING CALIBRATION CHECK

7.3.1 The 50 μg/L standard will be analyzed at the beginning of a sample sequence, after BFB has passed criteria, and before any samples or blanks.

7.3.2 The calibration check compounds' RRFs must be calculated and must be $\leq$25% different from the average RRF determined from the six point initial calibration before sample analysis may begin.

7.4 SAMPLES

7.4.1 All samples and blanks will be spiked with surrogates.

7.4.2 Surrogate recoveries will be calculated for each sample and blank.

7.4.2.1 If recoveries of one surrogate compounds is outside established limits, the sample must be reanalyzed. If reanalysis solves the problem, only report the reanalysis. If the sample still fails upon reanalysis document that reanalysis was performed and that surrogate recovery is matrix dependent.

7.4.2.2 Recovery ranges for the surrogates are:

COMPOUND	PERCENT RECOVERY
4-Bromofluorobenzene	86-115
1,2-Dichloroethane-d_4	76-114
Toluene-d_8	88-110

7.4.3 As an optional project specific quality control parameter, calculate matrix spike/matrix spike duplicate (MS/MSD) recoveries. MS/MSD should be performed on 5% of a batch, or 1 MS/MSD per 20 samples from the same project, when requested. The recovery ranges are based on SW846, 3rd edition guidelines. The MS/MSD compounds are:

Compound	Recovery Range %*	MSD-RPD*
1,1-dichloroethylene	61-146	14
toluene	76-125	13
trichloroethene	71-120	14
benzene	76-127	11
chlorobenzene	75-130	13

* These ranges are advisory ranges only. Failure to achieve this will not initiate reanalysis.

7.5 CONTROL CHARTS

Control charts shall be maintained for surrogate control analytes spiked in the method blank. Control charts are used to monitor the variations in the precision and accuracy of routine analyses and detect trends in these variations. Data from the laboratory analyses will be used to initially construct control charts. Data used in control charts shall not be adjusted for accuracy. Data from spiked QC samples within a lot will be compared to control chart limits to demonstrate that analyses of the lot are under control and in control data will be used to update the charts. Control charts are prepared for all of the surrogate analytes using the percent recovery data calculated according to the following equation:

$$\textit{Percent Recovery} = \frac{\textit{Found Concentration}}{\textit{Spiked Concentration}} \ x \ 100$$

Preparation of control charts requires the following data: An average percent recovery (X) of the surrogate in the two spiked QC samples (method blanks) in the analytical lot; and, a percent difference for the percent recovery of the surrogate in the two spiked QC samples (method blanks) in the analytical lot. Corrections to the QC Samples is required whenever an analyte is detected above the IDL in the Method Blank. The correction will be done based on the instrument response values and not the found values calculated from the calibration curve. (i.e., CLASS™ - ESE's computerized laboratory data managemnet system - data batches should specify a Method Blank correction "NONE".

8.0 REFERENCES

8.1 ESE SOP-ASM3241-001, Gas Chromatography/Mass Spectrometry (GC/MS) Determination of Volatile Organics (EPA 8240 and Appendix IX Compounds), Rev.

8.2 EPA Method 8240 - Test Methods for Evaluationg Solid Wastes, EPA SW 846, 3rd Edition, September 1986.

8.3 USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Document Number ILM01.8.

8.4 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

9.0 ATTACHMENTS

9.1 **Table of Compounds in each stock solution** - Attachment A

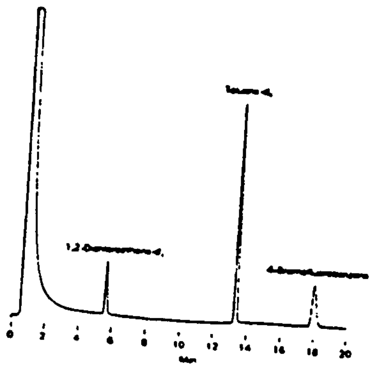
ATTACHMENT A

Table 2.3-1. Prepared Standard Mixtures.

SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

Purgeables Surrogate Standard Mix
Catalog No. 4-8876

This mixture contains 250µg/ml of each of the following components in methanol:



60/80 Carbopack™ B/1% SP™-1000, 8' x 1/8" SS, Col. Temp.: 100°C for 4 min., then to 220°C at 10°C/min., Inj. Temp.: 230°C, Det. Temp.: 250°C, Flow Rate: 30ml/min., N_2, Det.: FID (64 x 10⁻¹¹ AFS), Sample: 2µl Cat. No. 4-8876.

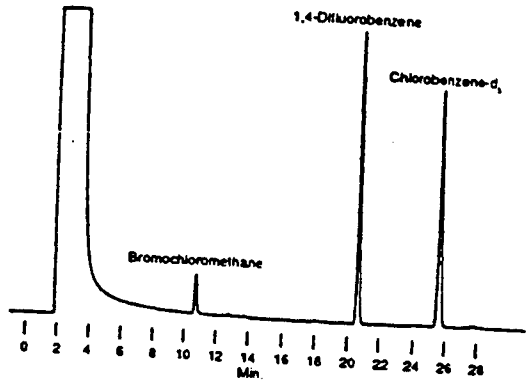
DS17458

SUPELCO
Bellefonte, PA

SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

VOA Internal Standard Mix
Catalog No. 4-8835

This mix contains 1000µg/ml of each of the following internal standards in methanol:



712-0396

60/80 Carbopack™ B/1% SP™-1000, 8' x 1/8" OD stainless steel, Col. Temp.: hold 3 min. at 45°C, then to 220°C at 8°C/min. and hold 15 min., Inj. Temp.: 200°C, Det. Temp.: 220°C, Flow Rate: 40ml/min., N_2, Det.: FID, Sens. 64 x 10⁻¹¹ AFS, Sample: 1µl of Cat. No. 4-8835.

DS11484D

SUPELCO
Bellefonte, PA

SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

Purgeable C (Gases)
Catalog No. 4-8853

This mixture contains the following constituents, each at 200µg/ml in methanol:

Chloromethane
Bromomethane
Vinyl chloride
Chloroethane

NOTE: Before opening, place the container in dry ice for ten minutes. After opening, transfer contents immediately to appropriate container and seal.

Store this mixture at -18°C.

DS13281D

SUPELCO
Bellefonte, PA

SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

Purgeable B Mix
Catalog No. 4-8852

This mixture contains 200µg/ml of each of the following components in methanol:

Benzene	
Bromodichloromethane	1,3-Dichloropropene*
Bromoform	Ethyl benzene
1,2-Dichloroethane	1,1,2,2-Tetrachloroethane
trans-1,2-Dichloroethylene	Toluene
	1,1,1-Trichloroethane

* 400µg/ml total dichloropropene, composed of
55.23 percent trans-1,3-dichloropropene
44.77 percent cis-1,3-dichloropropene as determined by FID

DS13281F

SUPELCO
Bellefonte, PA

Table 2.3-1. Prepared Standard Mixtures. (Continued)

SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

Purgeable A Mixture
Catalog Number 4-8851

This mixture contains 200µg/ml of each of the following components in methanol:

1. Methylene chloride
2. Trichlorofluoromethane
3. 1,1-Dichloroethylene
4. 1,1-Dichloroethane
5. Chloroform
6. Carbon tetrachloride
7. 1,2-Dichloropropane
8. Trichloroethylene
9. 1,1,2-Trichloroethane and Dibromochloromethane
10. 2-Chloroethyl vinyl ether *
11. Tetrachloroethylene
12. Chlorobenzene

60/80 Carbopack™ B/1% SP™-1000, 8' x 1/8" SS, Col. Temp.: hold 3 min. at 50°C, then to 220°C at 8°C/min., Inj. Temp.: 200°C, Det. Temp.: 250°C, Flow Rate: 30ml/min., He, Det.: Hall (halogen mode), Sens.: 20 x 10[?], Sample: 1µl of Cat. No. 4-8851.

* Due to the instability of 2-chloroethyl vinyl ether, we cannot guarantee the concentration of this component.

DS13181E
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DANGER-TOXIC-MAY BE FATAL IF SWALLOWED

Protocol analytical supplies, inc.

CAT# P-CLPV-D
LOT# 0921023C
DATE OPENED______
CLP BLEND D
FOR RESEARCH USE ONL

Contains 1000 ug/ml of the following in Methanol[67-56-1]:

Acetone	67-64-1
2-Butanone	78-93-3
Carbon Disulfide	75-15-0
cis-1,2-Dichloroethene	156-59-2
2-Hexanone	591-78-6
4-Methyl-2-Pentanone	108-10-1
Styrene	100-42-5
Vinyl Acetate	108-05-4
p-Xylene(500ug/ml)	106-42-3

Emil C. Lum
Signed

05-25-93
Date

Certificate of Analysis

DESCRIPTION: CLP VOLATILE MATRIX SPIKING SOLUTION

CATALOG NO.: 4-8399 LOT NO.: LA-33136

ANALYTE (1)	PERCENT PURITY (2)	WEIGHT CONCENTRATION (3)
BENZENE	99.0	250.3 +/- 1.3
CHLOROBENZENE	99.0	250.0 +/- 1.3
TOLUENE	99.0	250.3 +/- 1.3
TRICHLOROETHYLENE	99.0	250.6 +/- 1.3
1,1-DICHLOROETHYLENE	98.0	250.0 +/- 1.3

(1) Listed in alphabetical order.
(2) Determined by capillary GC-FID, unless otherwise noted.
(3) Quantity of analyte weighed into solution (ug/mL, +/- 0.5%). Weights of analytes less than 98% pure are corrected for impurities. Certified weights are not applicable to ampuls stored after opening, even if resealed.

Quality Assurance Manager

SUPELCO
SEPARATION TECHNOLOGIES

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN SOIL BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) - SW-846 8240
PACKED COLUMN METHOD - USAEC VMS-1
CAPILLARY COLUMN METHOD - USAEC VMS-2

TABLE OF CONTENTS

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN SOIL BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) - SW-846 8240 PACKED COLUMN METHOD - USAEC VMS-1 CAPILLARY COLUMN METHOD - USAEC VMS-2

1.0 SUMMARY AND APPLICATION

1.1 SUMMARY

This Standard Operating Procedure (SOP) follows EPA SW-846 protocols with additional quality control requirements applicable for the CLASS 1M analysis as specified in the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993). USEPA Contract Laboratory Program (CLP) Statement of Work for Organic Analysis, Document Number OLM01.8 allows for the analysis of VOA's by either packed or capillary columns. USAEC has required the assignment of two separate method numbers for the two columns but has agreed to the interchangeable use of either method since reporting limits have been designed to be consistent for both columns and method detection limits studies for each column support the reporting limits. Analytical capacity is the major reason for allowing the interchangeable use of either method. Data in the USAEC data base and control charts will distinguish between which method was used.

GC/MS tuning procedure and criteria follows guidelines as specified in OLM01.8. Additional QC requirements include analysis of two method blanks if the run is less than 12 hours and two thirds of the compounds must be within a 25% difference of the average RRF from daily calibration, all compounds must be within a 40% difference.

The method includes an optional hexadecane screening procedure. The extract is screened on a gas chromatograph/flame ionization detector (GC/FID) to determine the approximate concentration of organic constituents in the sample. For analysis an inert gas is bubbled through a mixture of reagent water and soil sample contained in a specifically designed purging chamber that is held at 40°C. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph (GC) is temperature programmed to separate the purgeables which are then detected with a mass spectrometer (MS).

1.2 APPLICATION

This SOP is applicable to the determination of volatile organic compounds in soil matrix by Gas Chromatography/Mass Spectrometry (GC/MS). Volatile (VOA) analysis of soil samples must be completed within 14 days of sampling date. The analytical method that follows is designed to analyze soil, from hazardous waste sites for the organic VOA compounds and Appendix IX compounds. The following compounds will be analyzed.

ANALYTE	ACRONYM	CAS Number
Acetone	ACET	67-64-1
Benzene	C6H6	71-43-2
Bromodichloromethane	BRDCLM	75-27-4
Bromoform	CH3BR	75-25-2
Bromomethane	ETHBR	74-83-9
2 - Butanone	MEK	78-93-3
Carbon Disulfide	CS2	75-15-0
Carbon Tetrachloride	CCL4	56-23-5
Chlorobenzene	CLC6H5	108-90-7
Chloroethane	C2H5CL	75-00-3
2-Chloroethyl Vinyl Ether	2CLEVE	110-75-8
Chlorform	CHCL3	67-66-3
Chloromethane	CH3CL	74-87-3
Dibromochloromethane	DBRCLM	124-48-1
1,1 - Dichloroethane	11DCLE	75-34-3
1,2 - Dichloroethane	12DCLE	107-06-2
1,2 - Dichloroethene, total	12DCE	540-59-0
1,1 - Dichloroethene	11DCE	75-35-4
1,2 - Dichloropropane	12DCLP	78-87-5
cis - 1,3 - Dichloropropene	C13DCP	10061-01-5
trans - 1,3 - Dichloropropene	T13DCP	10061-02-6
Ethylbenzene	ETC6H5	100-41-4
2 - Hexanone	MNBK	591-78-6
4 - Methyl - 2 - pentanone	MIBK	108-10-1
Methylene Chloride	CH2CL2	75-09-2
Styrene	STYR	100-42-5
1,1,2,2 - Tetrachloroethane	TCLEA	79-34-5
Tetrachloroethene	TCLEE	127-18-4
1,1,1 - Trichloroethane	111TCE	71-55-6
1,1,2 -Trichloroethane	112TCE	79-00-5
Trichloroethene	TRCLE	79-01-6
Toluene	MEC6H5	108-88-3
Vinyl Acetate	C2AVE	108-05-4
Vinyl Chloride	C2H3CL	75-01-4
Xylene, total	TXYLEN	-
1-Chloro-2,3-epoxypropene	-----	-
Acetonitrile	CH3CN	-
Ethylene oxide	ETOX	-
Methyl methacrylate	PLEXI	-

1.3 REPORTING LIMITS AND INITIAL CALIBRATION RANGES

Table 1.3-1 defines the reporting limits for the analytes analytes and the upper and lower initial calibration curve ranges. MDL studies are performed annually on both columns to confirm the validity of the chosen reporting limits following the procedure of 40 CFR Volume 4 No. 136, Appendix B.

1.4 INTERFERENCES

Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and the solvent vapors in the laboratory account for the majority of the contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and shipment. A trip blank is prepared from reagent water and carried through the sampling and handling protocol to serve as a check on such contamination. Contamination by carryover can occur whenever high level and low level samples are sequentally analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high purgeable levels, rinse it with distilled water, and then dry it in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

The laboratory where volatile analysis is performed should be completely free of solvents.

1.5 ANALYSIS RATE

Ten samples can be analyzed in an 8 hour shift.

1.6 SAFETY INFORMATION

Each compound should be treated as a potential health hazard. Inhalation of vapors, especially from neat volatile compounds should be avoided.

Table 1.3-1. Reporting Limits, and Upper and Lower Standard Range for Volatile Organic Compounds in Soil. Method 5030/8240

Parameter	Reporting Limit (ug/g)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)
Acetone	0.010	10	200
Benzene	0.010	10	200
Bromodichloromethane	0.010	10	200
Bromoform	0.010	10	200
Bromomethane	0.010	10	200
2 - Butanone	0.010	10	200
Carbon Disulfide	0.010	10	200
Carbon Tetrachloride	0.010	10	200
Chlorobenzene	0.010	10	200
Chloroethane	0.010	10	200
2-Chloroethyl Vinyl Ether	0.010	10	200
Chlorform	0.010	10	200
Chloromethane	0.010	10	200
Dibromochloromethane	0.010	10	200
1,1 - Dichloroethane	0.010	10	200
1,2 - Dichloroethane	0.010	10	200
1,2 - Dichloroethene, total	0.010	10	200
1,1 - Dichloroethene	0.010	10	200
1,2 - Dichloropropane	0.010	10	200
cis - 1,3 - Dichloropropene	0.010	10	200
trans - 1,3 - Dichloropropene	0.010	10	200
Ethylbenzene	0.010	10	200
2 - Hexanone	0.010	10	200
4 - Methyl - 2 - pentanone	0.010	10	200
Methylene Chloride	0.010	10	200
Styrene	0.010	10	200
1,1,2,2 - Tetrachloroethane	0.010	10	200
Tetrachloroethene	0.010	10	200
1,1,1 - Trichloroethane	0.010	10	200
1,1,2 -Trichloroethane	0.010	10	200
Trichloroethene	0.010	10	200
Toluene	0.010	10	200
Vinyl Acetate	0.010	10	200
Vinyl Chloride	0.010	10	200
Xylene, total	0.010	10	200
1-Chloro-2,3-epoxypropene	NA		
Acetonitrile	NA		
Ethylene oxide	NA		
Methyl methacrylate	NA		

NA = Information not available. A library search can be performed for the qualitative evaluation of samples for these compounds. No reporting limits have been established.
Note: Divide calibration standards by 1000 to convert to ug/g.

2.0 APPARATUS AND CHEMICALS

2.1 HARDWARE/GLASSWARE

2.1.1 Micro syringes: 10 uL and larger, 0.006 inch ID needle.

2.1.2 Disposable micropipettes: Various 5, 10, 20, 25, 100, 250 uL.

2.1.3 Syringe valve: Two-way, with Luer ends (three each), if applicable to the purging device.

2.1.4 Syringe: 5 mL, gas tight with shut-off valve.

2.1.5 Balance: Analytical, capable of accurately weighing $\pm$0.0001 g and a top-loading balance capable of weighing $\pm$0.1 g.

2.1.6 Glassware:

2.1.6.1 Bottle: 40 mL or 60 mL, screw cap, with Teflon cap liner.
2.1.6.2 Volumetric flasks: Class A with ground-glass stoppers.
2.1.6.3 Vials: 2 mL for GC autosampler.

2.1.7 Purge and trap device: The purge and trap device consists of three separate pieces of equipment; the sample purger, trap, and the desorber. Several complete devices are commercially available. This SOP was developed using Tekmar LSC 2000 concentrator interfaced to a Tekmar 2016 sixteen position autosampler or a Tekmar LSC 4000 concentrator interfaced to a Tekmar ALS ten position autosampler.

2.1.7.1 The sample purger must be designed to accept 5 mL samples with a water column at least 3 cm deep. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger must meet the design criteria specified in the method. Alternate sample purge devices may be utilized provided equivalent performance is demonstrated.

2.1.7.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. The trap must be packed to contain the following minimum lenghts of absorbents: 15 cm 2,6-diphenylene oxide polymer (Tenax-GC, 60/80 mesh) and 8 cm of silica gel (Davidson Chemical, 35/60 mesh, grade 15, or equivalent) and 1 cm 3% SP-2100, Supelco Catalog #2-0293.

2.1.7.3 The desorber should be capable of rapidly heating the trap to 220°C. The polymer section of the trap should not be heated higher than 220°C, and the remaining sections should not exceed 220°C during bakeout mode. The desorber design must meet these criteria.

2.1.7.4 The purge and trap device is coupled to a GC.

2.2 INSTRUMENTATION (GC/MS SYSTEM)

2.2.1 GC: An analytical system complete with a temperature programmable GC suitable for on-column injection and all required accessories including syringes, analytical columns, and gases.

2.2.2 Packed Column: 6 ft long x 0.1 in. ID glass, packed with 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent. Note: Capillary columns may be used for the analysis of volatile compounds by this method if the internal standards and surrogate compounds specified in this SOP are utilized and demonstrates the performance and QA/QC criteria contained in this SOP.

Capillary Columns: 30Mx0.53 mm, ID with Jet Seperator, 75Mx0.53 mm ID capillary direct.

2.2.3 MS: Capable of scanning from 35 to 300 amu every 3 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria when 50 ng of 4-bromoflurobenzene (BFB) is injected through the GC inlet. Alternately, 50 ng of bromofluorobenzene may be purged as an introduction method to determine instrument tuning compliance.

2.2.4 GC/MS: Any GC to MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the parameters of

interest and achieves all acceptable performance criteria may be used. GC to MS interfaces are constructed of all glass or glass-lined materials. Glass can be deactivated by silanizing with dichlorodimethylsilane.

2.2.5 Data System: A computer must be interfaced to the MS that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundance versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

2.2.6 The following systems are currently available for volatile compound analyses:

1. HP-1000/RTE-6V/M Computer
   a. HP-5985 GC/MS
   b. HP-5996 GC/MS

2. HP-3000 Computer HP-UX (425T)
   a. HP-5989 Engine

2.3 REAGENTS AND STANDARDS

2.3.1 Reagents:

2.3.1.1 Reagent Water: Reagent water is defined as water in which an interference is not observed at or above the EPA CRQLs of the parameters of interest. (Methylene Chloride, Acetone, Toluene and 2-Butanone $\leq$ 5 xCRQL). Reagent water is prepared by using double steam distilled water purged at 70°C with UPC grade helium overnight, and is held at constant temperature while purging continuously.

2.3.1.2 Methanol: Purge and trap grade.

2.3.2 Standards

2.3.2.1 Stock Standards:

2.3.2.1.1 Commercially prepared standards are used at the concentration certified by the manufacturer.

2.3.2.1.2 Store at -10°C to -20°C and protect from light.

2.3.2.1.3 Once a working solution is opened it may be used at most one week.

2.3.2.1.4 All standards should be replaced after six months or sooner if comparison with check standards indicates a problem (e.g., degradation, concentration).

2.3.2.1.5 Use Supelco prepared standard mixtures or other acceptable vendor. Table 2.3-1 in Attachment A identifies the compounds in each of the following mixtures:

1. Supelco Purgeable A: 4-8851 200 ug/mL
2. Supelco Purgeable B: 4-8852 200 ug/mL
3. Supelco Purgeable C: 4-8853 200 ug/mL
4. Protocol HSL Cat# P-CLPV-D 1000 ug/mL

2.3.2.1.6 Purgeables Internal Standard Mix: CLP Supelco 4-8835 or equivalent at 1000 ug each component in 1 mL of methanol. The three internal standards are bromochloromethane, chlorobenzene-d_5, and 1,4-difluorobenzene.

2.3.2.2 Working Standard Solutions:

Combine 200 uL of each A,B,C stocks at 200 ug/mL solution and 200 uL of dilute HSL (at 200 ug/ml) to make 800 uL of a 50 ug/mL solution. Make four more working standard solutions combining in the same manner and label as Notebook No.:, Page No.:, Entry No.: A,B,C,D, and E. Store in freezer between -10°C and -20°C and use each aliquot as needed (e.g., 441-85-2A, 441-085-2B, 441-85-2C). One mL of Protocol HSL(P-CLPV-D) at 1000 ug/mL is added to a 5

mL volumetric flask and diluted to mark to yeild a 200 ug/mL solution.

Standards must be stored in sealed vials at -10°C to -20°C and protected from light. If not so stored, they must be discarded after an hour.

2.3.2.3 Surrogate Standard Spiking Solution:

Supelco Purgeables Surrogate Standard Mix - CLP 4-8876 at 250 ug/mL each in methanol: bromofluorobenzene, 1,2-dichloroethane-d_4, and toluene-d_8 for waters. 200 uL of CLP 4-8876 surrogate mix is added to 800 uL of MeOH in a wheaton vial to yeild a 50 ug/mL solution.

2.3.2.4 Purgeable Organic Matrix Standard Spiking Solution/QC Reference **(PROJECT SPECIFIC, when requested)**. For sample matrix spikes, **when requested**, a 5 uL aliquot of the Supelco CLP volatile matrix spiking solution (Catalog No. 4-8399) is added to two 5 g portions from one sample chosen for spiking (each compound is 5 ug/g). Compounds are benzene, chlorobenzene, toluene, trichloroethylene, and 1,1-dichloroethylene.

2.3.2.5 Internal Standards Daily Spiking Solution

Dilute 500 uL of Stock Internal Standard Solution (Section 2.3.2.1.6) at 1,000 ug/mL to 10.0 mL with methanol to yield a 50 ug/mL daily spiking solution. Record in standards log and label.

2.3.2.6 Purchased neat BFB is purchased from Aldrich or an other acceptable vendor (density 1593 ug/uL). Prepare 20,000 ug/mL primary stock solution by adding 125 uL of neat BFB to methanol in a 10 mL volumetric and bring to mark. Prepare 50 ug/mL working solution by adding 25 uL of the primary stock to methanol in a 10 mL volumetric and bring to mark. Transfer to five or six ~2 mL sealed crimp top vials and store between -10°C and -20°C. Use each aliquot as needed. The primary is good for two years and the working solutions are good for six months.

2.3.2.7 Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10°C to -20°C in crimp-top bottles with Teflon liners and record and label as routine.

3.0 CALIBRATION

3.1 INITIAL CALIBRATION

Initial calibration occurs when a check of the daily calibration curve (performed every 12 hours) does not meet criteria. A percent difference of the daily (12 hour) relative response factor compared to the average relative response factor from the initial curve is calculated. A maximum percent difference of ≤ 25% is allowed for each compound flagged as "CCC" (see section 3.1.2.1 for stability/performance verification compounds). Preparation of initial calibration standards is described below. The analysis of the calibration standards performed as defined in Section 5.2 Analysis procedure.

3.1.1 Preparation of Initial Calibration Standards

Section 2.3.2.2 defines how to prepare the 50 ug/mL working standard solution. The following standards are prepared by adding the required volume of the working standard solution to 5 mL of standard water in the purge tube:

Std. Conc. ug/L	Volume of Stock uL
200	20
100	10
50	5
20	2
10	1
2	2*

* The 2 ug/L standard is prepared by using a 1:10 dilution of the working standard solution.

3.1.2 Analyze each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. The response factors for each compound are calculated from the area counts for the primary ion of the target

compounds compared to the area of the primary ion of the appropriate internal standard. Table 5.1-1 presents the primary and secondary ions for identification and the associated intenal standard for each compound. Calculate relative response factors (RRF) for each compound using equation 1.

$$\text{Eq 1: } RRF = \frac{(A_x C_{is})}{(A_{is} C_x)}$$

where:
- A_x = Area of the characteristic ion for the compound to be measured.
- A_{is} = Area of the characteristic ion for the specific internal standard.
- C_{is} = Concentration of the internal standard (ng/uL).
- C_x = Concentration of the compound to be measured (ng/uL).

3.1.2.1 Calculate an average RRF and relative standard deviation (RSD) for all compounds for the calibration standards . A system performance check must be made before this calibration curve is used. Five compounds [(the system performance check compounds (SPCC)] are checked for a minimum average RRF. These compounds (the SPCC) are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. RRFs must be $\geq$0.30, except bromoform $\geq$0.25. The response factors over the certified range will have less than 30-percent RSD for the calibration check compounds (CCC). If the RSD of the average RRF of any of the CCCs is greater than 30 percent, the initial calibration must be repeated. The CCC compounds are:

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl Chloride

3.2 DAILY CALIBRATION

The 50 ug/L standard (5 uL of the 50 ug/mL working stock) is used for daily calibration (see Section 3.1.1 for preparation). The analysis of the calibration standards is performed as defined in Section 5.0 following tuning procedures defined in Section 7.1. Use Equation 1, Section 3.1.2 to calculate RRF's for

each compound. The percent difference of the daily RRF compared to the average RRF from the initial curve must be $\leq$ 25% for two thirds of the compounds (including CCC's). All compounds must be within $\pm$ 40% except ketones, methylene chloride and chloroethane. If this criteria is not met, reanalyze the daily standard. If the daily standard fails again - perform a new initial six point curve.

3.2.1 A check of the calibration curve must be performed once every 12 hours during analysis. The minimum relative response factor for the system performance check compounds must be checked. If this criteria is met, the relative response factors of all compounds are calculated. A percent difference of the daily (12 hour) relative response factor compared to the average relative response factor from the initial curve is calculated. A maximum percent difference of $\leq$ 25% is allowed for each compound flagged as "CCC". Only after both these criteria are met can sample analysis begin.

3.2.2 Internal standard responses and retention times in all standards should be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system should be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards should be monitored and evaluated for each standard. If EICP area for any internal standard changes by more than a factor of two (-50 percent to +100 percent), the mass spectrometric system should be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning may be necessary.

4.0 SAMPLE HANDLING AND STORAGE

4.1 Samples will be collected using adequate dermal and inhalation protection and must follow Sections 3.3 and 3.4 of the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

4.2 Sample containers consist of 120 mL wide mouth amber-colored bottles with Teflon-lined septa. The sample bottles must be prepared according to Appendix C of the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

4.3 Samples should be kept chilled to 4°C and in the dark.

4.4 The holding time limit for completion of analysis is 14 days from the sampling date.

4.5 Verification of the calibration standards is based on the daily calibration control criteria, analysis of independent reference standards when available, and comparison of mass spectra with reference spectra from the Wiley/NIST database. If the 25 percent difference criteria cannot be met for the stability/performance check compounds reanalyzed the continuing calibration standard. If it stills fails then run initial calibration.

4.6 The verification of the surrogate spiking solution is based on control chart criteria.

5.0 PROCEDURE

Assemble a purge and trap device that meets the specification in Section 2.1.7. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 cm^3/min or in an oven. Daily, prior to use, condition the traps for 10 minutes while backflushing at 180°C with the column at 220°C. Connect the purge and trap device to a GC. The GC must be operated using temperature and flow rate parameters equivalent to those in Section 5.2. Tune the GC/MS system according to Section 7.1 by analyzing 50 ng of bromofluorobenzene (BFB) to meet the criteria listed in Section 7.1.4. Daily calibration of the purge and trap-GC/MS system is performed using internal standards (Section 3.2). Analyze samples as discussed below following optional screening Section 5.16. Table 5.1-1 summarizes the primary and secondary quantitation ions and the appropriate internal standard for each compound. Section 6.1 discusses compound identification. Section 6.2 discusses calculations for final concentrations for the identified compounds. Section 6.3 discusses tentatively identified compound searches. When the medium level method is required see the protocol defined in Attachment A.

5.1 GC/MS Operating conditions:

These performance test required the following instrumental parameters:

Electron Energy:	70 Volts (nominal)
Mass Range:	35 - 300 amu
Scan Time:	To give at least 5 scans per peak and not to exceed 3 seconds per scan.

5.2 Analytical procedure for water sample analysis:

5.2.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

5.2.2 Operating conditions for the GC packed column instruments (Section 2.2.6.1.a and b): Carbopak B (60/80 mesh) with 1 percent SP-1000 packed in a 1.8 m by 2 mm ID glass column to a jet separator with helium carrier gas at a flow rate of 30 cm^3/min. Column temperature is isothermal at 35°C for 3 minutes and then programmed @ 8°C/min to 225°C (220°C for instrument 2.2.6.1.b) and held for 15 minutes. Injector temperature is 200-225°C. Source temperature is set according to the manufacturer's specifications. Transfer line temperature is 230°C.

Operating conditions for the GC capillary column instruments (Section 2.2.5.2.a): A 75 m DB624 fused silica wide-bore capillary column 3um film thickness directly conected to MS. Column initial temperature is isothermal at 35°C for 4 minutes and then programmed @ 8°C/min to 175°C and held for 15 minutes. Injector temperature is 200-225°C. Source temperature is set according to the manufacturer's specifications. Transfer line temperature is 230°C.

5.3 After achieving the key ion abundance criteria for BFB, calibrate the system daily.

5.4 Adjust the purge gas (helium) flow rate to 25-40 cm^3/min. Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

5.5 The low level soil method is based on a heated purge of a soil/sediment sample mixed with reagent water containing the surrogate and the internal standards. Analyze all method blanks and standards under the same conditions as the samples.

5.6 The GC/MS system must be set up as in Section 5.1 through 5.4. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration standard must be prepared and used for the quantitation of all samples analyzed with the low level method. Initial and continuing calibrations are performed by adding standards in methanol to reagent water and purging at 40°C.

5.7 To prepare the reagent water containing the surrogates and the internal standards, remove the plunger from a 5 mL "Luerlock" type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5 mL. Allow the organic free water in the syringe to cool before the addition of surrogates and internal standards. Add 5 uL of the surrogates spiking solution and 5 uL of the internal standard solution to the syringe through the valve.

5.8 The sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh 5 g (wet weight) into a tared purge device. Use a top loading balance. Note and record the actual weight to the nearest 0.1 g.

5.9 Add the spiked reagent water to the purge device and connect the device to the purge and trap system. Note: Steps 5.6 and 5.7 must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

5.10 Heat the sample to 40°C and purge the sample for 11 minutes.

5.11 Proceed with the analysis as outlined in Steps 5.14 through 5.20.

5.12 To prepare a matrix spike and matrix spike duplicate for low level soils/sediment, add 5 uL of the matrix spike solution (Section 2.3.2.4) to the 5 mL of water added to each of the two aliquots of the soil from the sample chosen for spiking. The concentration for a 5 g sample would be equivalent to 0.050 ug/g of each matrix spike compound.

5.13 Close both valves and purge the sample for 11.0 $\pm$ 0.1 minutes at ambient temperature.

5.14 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the GC temperature program. Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 220°C while backflushing the trap with an inert gas between 20 and 60 cm^3/min for four minutes.

5.15 While the trap is being desorbed into the GC, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water to avoid carryover of pollutant compounds.

5.16 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed, however the higher temperature will shorten the useful life of the trap. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample. Alternative trap is baked out @ 260°C.

5.17 If the initial analysis of a sample or a dilution of a sample has concentration of compounds that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. NOTE: For total xylenes, where three isomers are quantitated as two peaks, the calibration range of <u>each peak</u> should be considered separately (e.g., a diluted analysis is <u>not</u> required for total

xylenes unless the concentration of either peak separately exceeds 200 ug/L). Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is used, document the reasons. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

5.18 All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

5.19 Optional VOA GC/FID screen - weigh 10 gm. of soil into a 40 mL VOA vial. Fill with purged H_2O to the neck of the vial and top off with hexadecane. Shake for twenty minutes on a wrist action shaker. Remove from the wrist action shaker and pipette off the hexadecane solvent layer, i.e. the top layer, into a crimp top autosampler vial. Screen by GC/FID.

5.19.1 Prepare a standard by spiking 5 uL of a 25 mg/mL standard solution containing benzene, chlorobenzene, 1,1 dichloroethene, toluene, and trichloroethene into 40 mL of reagent water in a VOA bottle. Add 2 mL of hexadecane and extract as described in Section 5.21 (Concentration = 62.5 ng/uL).

5.19.2 GC/FID Screen - Inject 3 uL of the 62.5 ng/uL VOA standard described in 5.19.1. Inject the sample screen extract and compare the response of the peaks to the standard response. The sample will be analyzed neat by GC/MS when no peaks are detected or any peaks are less than one-half the peak responses of the standard. Appropriate dilutions for GC/MS analysis is performed when any peaks are greater than one-half of the peak responses of the standard.

5.19.3 For low level soil, less than five grams can be used, but no lower than one gram. This limits the effective dilution for low level soils to 5X. For medium level soils, less than 100uL of methanol extract is added to the five mL of water to adjust for dilutions.

Table 5.1-1. **Quantitation Ions and Internal Standards.**

Analyte	Primary Ion	Secondary Ion(s)	Internal* Standard
Acetone	43	58	A
Benzene	78	--	B
Bromodichloromethane	83	85	B
Bromomethane	94	96	A
2-Butanone	72	57	A
Carbon disulfide	76	78	A
Bromoform	173	171,175,250	B
Carbon Tetrachloride	117	119,121	B
Chlorobenzene	112	114	C
Chloromethane	50	52	A
2-Chloroethylvinyl ether	106	63,65	B
Chloroform	83	85	A
Chloroethane	64	66	A
Dibromochloromethane	129	208,206	B
1,1-Dichloroethane	63	65,83,85	A
1,2-Dichloroethane	62	64,100,98	A
1,1-Dichloroethene	96	61,98	A
1,2-Dichloroethene	96	61,98	A
1,2-Dichloropropane	63	65,114	B
cis-1,3-Dichloropropene	75	77	B
trans-1,3-Dichloropropene	75	77	B
Ethylbenzene	106	91	C
2-Hexanone	43	58,57,100	C
Methylene Chloride	84	48,51,86	A
4-Methyl-2-Pentanone	43	58,100	C
Styrene	104	78,103	C
1,1,2,2-Tetrachloroethane	83	83,131,135,166	C
Tetrachloroethene	164	129,131,166	C
Toluene	92	91	C
1,1,1-Trichloroethane	97	99,117,119	B
1,1,2-Trichloroethane	97	83,85,99,132,134	B
Trichloroethene	130	95,97,132	B
Trichlorofluoromethane	101	103	A
Vinyl Acetate	43	86	B
Vinyl Chloride	62	64	A
o-Xylene	106	91	C
m-Xylene	106	91	C
p-Xylene	106	91	C
4-Bromofluorobenzene	95	174,176	C
1,2-Dichloroethane-D(4)	65	102	A
Toluene-D(8)	98	70,100	C
Internal Standards:			
Bromochloromethane	128	49,130,51	A
1,4-Difluorobenzene	114	63,88	B
Chlorobenzene	117	82,119	C

6.0 IDENTIFICATION, QUANTITATION, AND TENTATIVE IDENTIFICATIONS

6.1 COMPOUND IDENTIFICATION

6.1.1 The compounds shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compounds. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time (RRT) as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

6.1.1.2 For establishing correspondence of the GC RRT, the sample component RRT must compare within $\pm$ 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

6.1.1.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the GC/MS meets the daily tuning requirements for BFB. These standard spectra may be obtained from the run used to obtain reference RRTs.

6.1.1.4 The requirements for qualitative verification by comparison of mass spectra are as follows:

6.1.1.4.1 All ions present in the standard mass spectra at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.

6.1.1.4.2 The relative intensities of ions specified in Section 3.11 must agree within $\pm$ 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50 % in the standard spectra, the

corresponding sample abundance must be between 30 and 70 %).

Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. All compounds meeting the identification criteria must be reported with their spectra.

6.1.1.5 If a compound cannot be verified by all of the criteria in Section 6.1.1.4, but in the technical judgement of the mass spectral interpretation specialist, the identification is correct, then report that identification and proceed with quantitation in Section 6.2.

6.2 Quantitative Determinations

6.2.1 Components identified shall be quantitated by the internal standard method. The internal standard used shall be that which is listed. The EICP area of the characteristic ions of analytes listed are used.

6.2.2 Internal standard responses and retention times in all standards should be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12 hour) calibration standard, the chromatographic system should be inspected for malfunctions, and corrections made as required. The EICP of the internal standards should be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50 to +100 %), the MS system should be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning may be necessary.

6.2.3 The RRF from the daily standard analysis is used to calculate the concentration in the sample. Use the RRF as determined in section 3.5 and the equations below.

$$\text{Concentration ug/g} = \frac{(A_x)(I_s)}{(A_{is})(RRF)(W_0)(100\text{-}\%M)}$$

A_x = area of the characteristic ion for the compound to be measured,
A_{is} =area of the characteristic ion for the specific internal standard,
I_s = amount of internal standard added in micrograms (ug),
W_0 = Weight of soil purged in g, and
%M = Percent moisture of soil sample.

6.2.4 An estimated concentration for components tentatively identified shall be quantitated by the internal standard method. For quantitation, the nearest internal standard free of interferences shall be used.

6.2.4.1 The formula for calculating concentrations is the same as in Section 6.2.3. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A RRF of one is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

6.2.5 Xylenes (o-, m-, and p- isomers) are to be reported as Xylenes (total). Since o- and p-Xylene overlap, the Xylenes must be quantitated as m-Xylene. The concentration of all Xylene isomers must be added together to give the total.

6.2.6 1,2-Dichloroethene (trans and cis steroisomers) are to be reported as 1,2-Dichloroethene (total). The concentrations of both isomers must be added together to give the total, especially for the capillary column method option where isomers are resolved.

6.2.7 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits and report.

6.2.7.1 Calculation for surrogate recovery:

$$\% \ Surrogate\ Recovery = \frac{Q_d}{Q_a} \times 100\%$$

where: Q_d = quantity determined by analysis, and
Q_a = quantity added to sample.

6.2.7.2 If recovery is not within limits, the following is required:

6.2.7.2.1 Check to be sure there are no errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance.

6.2.7.2.2 Reanalyze the sample if none of the above reveal a problem.

6.2.7.3 If the reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only report data from the analysis with surrogate spike recoveries within the limits. This is considered the initial analysis and shall be reported as such on all data deliverables, however all runs are included on run logs and identified as why the run was not used. All runs will be included in data package.

6.2.7.4 If the reanalysis of the sample does not solve the problem (i.e., surrogate recoveries are outside the limits for both analysis), then check the surrogates in the method blank and spike check. If the surrogates in the method blank and spike check are within limits, qualify the data.

6.2.7.5 If the sample with surrogate recoveries outside the limits is the sample used for the matrix spike and matrix spike duplicate, and the surrogate recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), then the sample, matrix spike, and matrix spike duplicate do not require reanalysis. Document the similarity in surrogate recoveries.

6.2.7.6 ESE's QA Manual lists the accuracy, precision and reporting limit data of the Appendix IX organic volatile compounds that were validated using this method.

6.3 TENTATIVELY IDENTIFIED COMPOUND SEARCH

6.3.1 A library search shall be executed for sample components for the purpose of tentative identification. For this purpose, the 1989 release of the NIST Mass Spectral Library (or more recent release), containing 130,000 spectra, shall be used. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

6.3.2 All nonsurrogate non target organic compounds with responses greater than 10 percent of the internal standard shall be tentatively identified via a forward search of the Wiley/NIST mass spectral library. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

6.3.3 Guidelines for making tentative identification are as follows:

6.3.3.1 Relative intensities of major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum).

6.3.3.2 The relative intensities of the major ions should agree within $\pm$ 20 percent. (Example: For an ion with an abundance of 50 % of the standard spectra, the corresponding sample ion abundance must be between 30 and 70 %).

6.3.3.3 Molecular ions present in reference spectrum should be present in sample spectrum.

6.3.3.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

6.3.3.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

6.3.4 If in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

7.0 DAILY QUALITY CONTROL

7.1 TUNING

7.1.1 Prior to the analyses of any samples, blanks, or calibration standards, the Contractor must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing p-bromofluorobenzene (BFB).

7.1.2 The analysis of the instrument performance check solution is performed as follows:

7.1.2.1 A 1 uL injection of the working BFB solution (Section 2.3.2.6) (50 ng of BFB) into the GC/MS for instruments listed in 2.2.6.1 and 2.2.6.2.

7.1.2.2 Add 1 uL of the working BFB solution (Section 2.3.2.6) (50 ng of BFB) to 5.0 mL of reagent water and analyzing the resulting solution as if it were an environmental sample (see sample analysis procedure) on instruments 2.2.6.3 and 2.2.6.4.

7.1.2.3 BFB may not be analyzed simultaneously with a calibration standard.

7.1.3 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background

6.3.3.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

6.3.4 If in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

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7.1.2.2 Add 1 uL of the working BFB solution (Section 2.3.2.6) (50 ng of BFB) to 5.0 mL of reagent water and analyzing the resulting solution as if it were an environmental sample (see sample analysis procedure) on instruments 2.2.6.3 and 2.2.6.4.

7.1.2.3 BFB may not be analyzed simultaneously with a calibration standard.

7.1.3 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background

7.2 METHOD BLANK

7.2.1 Method blanks must be analyzed for each 12 hours of sample run.

7.2.2 Two method blanks will be supplied with each batch of samples. If the analytical sample run is less than 12 hours, both method blanks must be analyzed.

7.3 CONTINUING CALIBRATION CHECK

7.3.1 The 50 μg/L standard will be analyzed at the beginning of a sample sequence, after BFB has passed criteria, and before any samples or blanks.

7.3.2 The calibration check compounds' RRFs must be calculated and must pass criteria specified in 3.2.

7.4 SAMPLES

7.4.1 All samples and blanks will be spiked with surrogates.

7.4.2 Surrogate recoveries will be calculated for each sample and blank.

7.4.2.1 If recoveries of one surrogate compounds is outside established limits, the sample must be reanalyzed. If reanalysis solves the problem, only report the reanalysis. If the sample still fails upon reanalysis document that reanalysis was performed and that surrogate recovery is matrix dependent.

7.4.2.2 Recovery ranges for the surrogates are:

COMPOUND	PERCENT RECOVERY
4-Bromofluorobenzene	74-121
1,2-Dichloroethane-d_4	70-121
Toluene-d_8	81-117

7.4.3 As an **optional** project specific quality control parameter, calculate matrix spike/matrix spike duplicate (MS/MSD) recoveries. MS/MSD should be performed on 5% of samples in a batch, or 1 MS/MSD per 20 samples from the same project, **when requested**. The recovery ranges are based on SW846, 3rd edition guidelines. The MS/MSD compounds are:

Compound	Recovery Range %*	MSD-RPD*
1,1-Dichloroethene	59-172	22
Toluene	59-139	21
Trichloroethene	62-137	24
Benzene	66-142	21
Chlorobenzene	60-133	21

* These ranges are advisory ranges only. Failure to achieve this will not initiate reanalysis.

7.5 CONTROL CHARTS

Control charts shall be maintained for surrogate control analytes spiked in the method blank. Control charts are used to monitor the variations in the precision and accuracy of routine analyses and detect trends in these variations. Data from the laboratory analyses will be used to initially construct control charts. Data used in control charts shall not be adjusted for accuracy. Data from spiked QC samples within a lot will be compared to control chart limits to demonstrate that analyses of the lot are under control and in control data will be used to update the charts. Control charts are prepared for all of the surrogate analytes using the percent recovery data calculated according to the following equation:

$$Percent\ Recovery = \frac{Found\ Concentration}{Spiked\ Concentration} \times 100$$

Preparation of control charts requires the following data: An average percent recovery (X) of the surrogate in the two spiked QC samples (method blanks) in the analytical lot; and, a percent difference for the percent recovery of the surrogate in the two spiked QC samples (method blanks) in the analytical lot. Corrections to the QC Samples is required whenever an analyte is detected above the IDL in the Method Blank. The correction will be done based on the instrument response values and not the found values calculated from the calibration curve. (i.e., CLASS™ - ESE's computerized laboratory data management system - data batches should specify a Method Blank correction "NONE".

8.0 REFERENCES

8.1 ESE SOP-ASM3241-001, Gas Chromatography/Mass Spectrometry (GC/MS) Determination of Volatile Organics (EPA 8240 and Appendix IX Compounds), Rev.

8.2 EPA Method 8240 - Test Methods for Evaluationg Solid Wastes, EPA SW 846, 3rd Edition, September 1986.

8.3 USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Document Number ILM01.8.

8.4 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

9.0 ATTACHMENTS

9.1 Table of Compounds in each stock solution - Attachment A

9.1 Medium Level soil method - Attachment B

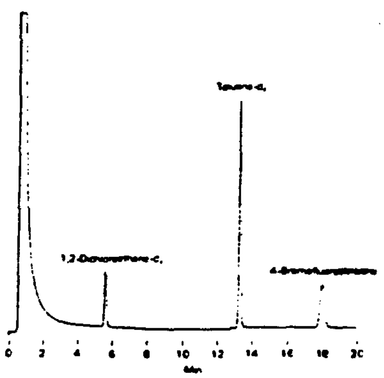
ATTACHMENT A

Table 2.3-1. Prepared Standard Mixtures.

SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

Purgeables Surrogate Standard Mix
Catalog No. 4-8876

This mixture contains 250μg/ml of each of the following components in methanol:



60/80 Carbopack™ B/1% SP™-1000, 8' x 1/8" SS, Col. Temp.: 100°C for 4 min., then to 220°C at 10°C/min., Inj. Temp.: 230°C, Det. Temp.: 250°C, Flow Rate: 30ml/min., N_2, Det.: FID (64 x 10⁻¹¹ AFS), Sample: 2μl Cat. No. 4-8876

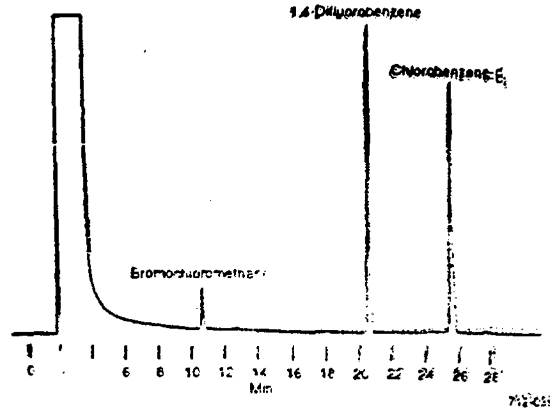
DS17856

SUPELCO
Bellefonte, PA

SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

VOA Internal Standard Mix
Catalog No. 4-8835

This mix contains 1000μg/ml of each of the following internal standards in methanol:



60 ... 1000, 8' x 1/8" OD stainless steel, Col. Temp.: ... and hold 15 min., Inj. Temp.: 200°C, Det. Temp.: ... FID, Sens.: ... x 10⁻¹¹ AFS, Sample: ...

SUPELCO
Bellefonte, PA

SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

Purgeable C (Gases)
Catalog No. 4-8853

This mixture contains the following constituents each at 200μg/ml in methanol.

Chloromethane
Bromomethane
Vinyl chloride
Chloroethane

NOTE: Before opening, place the container in dry ice for ... minutes. After opening, transfer contents immediately to appropriate container and seal.

Store this mixture at -18°C.

DS155...

SUPELCO
Bellefonte, PA

SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

Purgeable B Mix
Catalog No. 4-8852

This mixture contains 200μg/ml of each of the following components in methanol.

Benzene	1,3-Dichloropropene*
Bromodichloromethane	Ethylbenzene
Bromoform	1,1,2,2-Tetrachloroethane
1,2-Dichloroethane	Toluene
trans-1,2-Dichloroethylene	1,1,1-Trichloroethane

* 400μg/ml total dichloropropene, composed of
[illegible] percent trans-1,3-dichloropropene
[illegible] percent cis-1,3-dichloropropene as determined by FID

SUPELCO
Bellefonte, PA

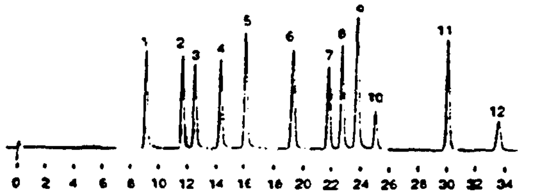
Table 2.3-1. Prepared Standard Mixtures. (Continued)

SAVE THIS DATA SHEET!
It Contains Important Information About This Product.

Purgeable A Mixture
Catalog Number 4-8851

This mixture contains 200µg/ml of each of the following components in methanol:

1. Methylene chloride
2. Trichlorofluoromethane
3. 1,1-Dichloroethylene
4. 1,1-Dichloroethane
5. Chloroform
6. Carbon tetrachloride
7. 1,2-Dichloropropane
8. Trichloroethylene
9. 1,1,2-Trichloroethane and Dibromochloromethane
10. 2-Chloroethyl vinyl ether *
11. Tetrachloroethylene
12. Chlorobenzene



712-0221

60/80 Carbopack™ B/1% SP™-1000, 8' x 1/8" SS, Col. Temp.: hold 3 min. at 50°C, then to 220°C at 8°C/min., Inj. Temp.: 200°C, Det. Temp.: 250°C, Flow Rate: 30ml/min., He, Det.: Hall (halogen mode), Sens.: 20 x 10², Sample: 1µl of Cat. No. 4-8851

* Due to the instability of 2-chloroethyl vinyl ether, we cannot guarantee the concentration of this component.

DS13181E

SUPELCO
Bellefonte, PA

1st methanol
DANGER-TOXIC-MAY BE FATAL IF SWALLOWED

Protocol
analytical supplies, Inc.

CAT# P-CLPV-D
LOT# 0921023C
DATE OPENED ______
CLP BLEND D
FOR RESEARCH USE ONL

Contains 1000 ug/ml of the following in Methanol(67-56-1):

Acetone	67-64-1
2-Butanone	78-93-3
Carbon Disulfide	75-15-0
cis-1,2-Dichloroethene	156-59-2
2-Hexanone	591-78-6
4-Methyl-2-Pentanone	108-10-1
Styrene	100-42-5
Vinyl Acetate	108-05-4
p-Xylene(500ug/ml)	106-42-3

Signed: Carol C. [illegible] Date: 05-25-93

Certificate of Analysis

DESCRIPTION CLP VOLATILE MATRIX SPIKING SOLUTION

CATALOG NO 4-8355 LOT NO [illegible]

ANALYTE (1)	PERCENT PURITY (2)	WEIGHT CONCENTRATION (3)
BENZENE	99.0	250.3 +/- 1.3
CHLOROBENZENE	99.0	250.0 +/- 1.3
TOLUENE	99.0	250.3 +/- 1.3
TRICHLOROETHYLENE	99.0	250.6 +/- 1.3
1,1-DICHLOROETHYLENE	99.0	250.0 +/- 1.3

(1) Listed in alphabetical order.
(2) Determined by capillary GC-FID, unless otherwise noted.
(3) Quantity of analyte weighed into solution (ug/mL, +/- 0.5%). Weights of analytes less than 98% pure are corrected for impurities. Certified weights are not applicable to ampuls stored after opening, even if resealed.

James M. Schneider
Quality Assurance Manager

SUPELCO
SEPARATION TECHNOLOGIES

VOA HP 5987
1993
MDL WATER (ug/l)

Compound Name	Target Level	rep.1	rep.2	rep.3	rep.4	rep.5	rep.6	rep.7	Standard Dev.	MDL
Chloromethane	2	2.00	1.97	2.10	2.17	2.31	2.22	2.15	0.12	0.38
Bromomethane	2	3.21	2.98	2.91	2.95	3.00	2.99	2.67	0.16	0.50
Dichlorodifluoromethane	400	428.64	481.78	408.63	464.85	446.39	655.20	695.15	114.84	360.93
Vinyl Chloride	2	1.98	2.44	2.49	2.43	2.55	2.60	2.31	[illegible]	0.65
Ethanol	1000	1283.5	1192.8	1195.9	1050.8	1226.4	1130.6	1221.5	75.17	236.26
Chloroethane	2	1.74	1.94	1.96	1.95	1.96	1.86	1.85	0.08	0.26
Acetonitrile	5	4.46	2.70	4.04	5.22	4.32	4.63	1.72	1.22	3.84
Iodomethane	5	4.86	4.82	4.87	4.71	4.66	4.85	4.86	0.08	0.26
Methylene Chloride (MBSUB)	2	1.86	1.84	1.84	1.91	1.72	1.87	1.81	0.06	0.19
Acetone (MBSUB)	10	10.38	8.12	11.74	7.83	7.21	9.40	8.47	1.59	5.00
Acrolein	5	3.19	2.47	3.37	2.65	3.15	3.33	3.58	0.40	1.26
Carbon Disulfide	2	1.92	2.06	1.92	1.93	1.97	1.94	1.83	0.07	0.22
Acrylonitrile	5	2.03	2.94	2.67	3.06	3.39	3.48	2.73	0.49	1.54
Propionitrile	5	3.43	1.86	2.64	3.32	1.86	2.63	3.10	0.65	2.03
Trichlorofluoromethane	5	1.81	1.85	2.01	1.96	1.90	1.94	1.76	0.09	0.28
3-Chloropropene	5	4.70	4.68	4.66	1.94	4.55	2.42	3.67	1.17	3.69
1,1-Dichloroethene	2	1.65	1.74	1.74	1.71	1.87	1.83	1.68	0.08	0.25
1,1-Dichloroethane	2	1.74	1.92	1.85	1.84	1.86	1.84	1.68	0.08	0.25
1,2-Dichloroethene (total)	2	1.61	1.68	1.72	1.80	1.68	1.71	1.58	0.07	0.23
Diethyl ether	2	1.70	1.81	1.67	1.19	1.84	1.48	1.43	0.23	0.73
Chloroform	2	2.31	2.12	2.26	2.23	2.34	2.18	2.15	0.08	0.26
112-Trich-122-trifl-ethane	2	5.26	5.32	5.32	5.33	5.30	4.54	5.24	0.29	0.90
1,2-Dichloroethane	2	1.74	1.74	1.85	1.62	1.96	1.81	1.83	0.11	0.34
2-Butanone	10	12.41	8.08	8.19	7.33	10.90	9.12	8.17	1.83	5.74
Dibromomethane	5	4.78	5.06	5.00	4.82	4.92	4.95	4.82	0.10	0.33
Methacrylonitrile	5	4.17	3.80	4.01	3.93	3.88	3.65	3.68	0.18	0.58
1,4-Dioxane	1000	886.43	986.38	982.91	939.93	956.86	965.53	1082	59.22	186.14
1,1,1-Trichloroethane	2	2.32	2.22	2.18	2.41	1.74	2.07	1.61	0.30	0.94
Carbon Tetrachloride	2	1.54	1.71	1.83	1.74	1.65	1.78	1.44	0.14	0.43

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: DETERMINATION OF ORGANOCHLORINE PESTICIDES AND PCBs IN ENVIRONMENTAL WATER SAMPLES (SW-846 METHOD 3520/8081) USAEC METHOD - CAPILLARY COLUMN PST1

TABLE OF CONTENTS

December 7, 1993

TITLE: DETERMINATION OF ORGANOCHLORINE PESTICIDES AND PCBs IN ENVIRONMENTAL WATER SAMPLES (SW-846 METHOD 3520/8081) USAEC METHOD - CAPILLARY COLUMN PST1

1.0 SUMMARY AND APPLICATION

1.1 Summary

NOTE: THIS METHOD IS APPROVED FOR CAPILLARY COLUMN AT THE TIME OF PRINTING. WHEN THE MEGABORE MDL STUDY IS SUBMITTED AND APPROVED, THEN THIS STATEMENT WILL BE REMOVED, THE METHOD HEADER CONVERTED TO REVISION 1, AND A NEW COPY PRINTED AND DISTRIBUTED.

This Standard Operating Procedure (SOP) follows EPA SW-846 protocols with additional quality control requirements applicable for the CLASS 1P analysis as specified in the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993). The analysis procedure is based on SW-846 method 8080 AND 8081 and the sample extraction and preparation method is based on SW-846 method 3520 (Continuous Liquid/Liquid extraction). The method determination of retention windows and spike analytes are based on the USEPA Contract Laboratory Program (CLP) Statement of Work for Organic Analysis, Document Number OLM01.8 SOW, which differs from SW-846 protocols.

CLP criteria allows for the analysis of OCP/PCB's by either capillary or megabore columns. USAEC has required the assignment of two separate method numbers for the two columns but has agreed to the interchangeable use of either method since reporting limits have been designed to be consistent for both columns and method detection limits studies for each column support the reporting limits. Analytical capacity is the major reason for allowing the interchangeable use of either method. Data in the USAEC data base and control charts will distinguish between which method was used.

A measured volume of sample (1000 mL) is continously extracted with methylene chloride using a continuous liquid-liquid extractor. The methylene chloride is exchanged for hexane, then concentrated to a final volume of 5 milliliters (mL). The extract is then analyzed using a Gas Chromatograph equipped with Electron Capture Detector. Chromatographic conditions are described which permit the separation and measurement of the analytes in the hexane extract. Identification is performed using

retention times, and quantitation is performed using external standard curves.

1.2 Applicaton

1.2.1 This method is applicable to all environmental water samples.

1.2.2 This method is applicable to the quantitative determination of the following organochlorine pesticides and PCBs in environmental water samples listed in Table 1.2-1.

1.2.3 The reporting limit and the lower and upper standard range for this method are listed in Table 1.2-2.

1.2.4 Interferences

1.2.4.1 Interferences by phthalate esters can pose major problems in pesticide analysis. The interference can usually be minimized by preventing contact of reagents, glassware, apparatus, and samples with any plastic materials.

1.2.4.2 Solvents, reagents, glassware, and other sample processing equipment may yield chromatograms with interfering peaks. All reagents, glassware, and sample handling equipment must be demonstrated to be free from interferences which have retention times equal to those of the compounds of interest.

1.2.5 Analysis Rate

After instrument calibration, one analyst can analyze 20 samples in a 24-hour day. One analyst can perform approximately 20 extractions in an 8-hour day.

1.2.6 Health and Safety Information

The target compounds in this method are toxic. The preparation of all standards should be performed in a laboratory hood. Adequate dermal protection must be used when handling samples and standards.

Table 1.2-1. USAEC Acronyms and CAS Numbers for OCP's and PCB's (page 1 of 2).

Single Component Pesticides	Acronyms	CAS Number
Aldrin	ALDRN	309-00-2
Alpha-BHC	ABHC	319-84-6
Beta-BHC	BBHC	319-85-7
Delta-BHC	DBHC	319-86-8
Gamma-BHC (Lindane)	LIN	58-89-9
Chlordane (alpha)	ACLDAN	5103-71-9
Chlordane (gamma)	GCLDAN	5566-34-7
4,4'-DDD	PPDDD	75-54-8
4,4'-DDE	PPDDE	72-55-9
4,4'-DDT	PPDDT	50-29-3
Dieldrin	DLDRN	60-57-1
Endosulfan I	AENSLF	959-98-8
Endosulfan II	BENSLF	33212-65-9
Endosulfan Sulfate	ESFSO4	1031-07-8
Endrin	ENDRN	72-20-8
Endrin Aldehyde	ENDRNA	7421-93-4
Endrin Ketone	ENDRNK	53494-70-5
Heptachlor	HPCL	76-44-8
Heptachlor Epoxide	HPCLE	1024-57-5
Methoxychlor	MEXCLR	72-43-5

Table 1.2-1. USAEC Acronyms and CAS Numbers for OCP's and PCB's (page 2 of 2).

Multi-Component Pesticides	Acronym	CAS Number
Technical Chlordane	CLDAN	57-74-9
Toxaphene	TXPHEN	80001-35-2
Aroclor 1016	PCB016	12674-11-2
Aroclor 1221	PCB221	1104-28-2
Aroclor 1232	PCB232	11141-16-5
Aroclor 1242	PCB242	53469-21-9
Aroclor 1248	PCB248	12672-29-6
Aroclor 1254	PCB254	11097-69-1
Aroclor 1260	PCB260	11096-82-5

Table 1.2-2. Reporting Limits, and Lower and Upper Standard Range for Organochlorine Pesticides in Water by EPA Method 8080/8081 (page 1 of 2).

Parameter	Reporting Limit (ug/L)[1]	Lower Standard Range (ng/mL)	Upper Standard Range (ng/mL)
Aldrin	0.005	1.0	100.0
Alpha-BHC	0.005	1.0	100.0
Beta-BHC	0.005	1.0	100.0
Delta-BHC	0.005	1.0	100.0
Gamma -BHC (Lindane)	0.005	1.0	100.0
Chlordane (alpha)	0.005	1.0	100.0
Chlordane (gamma)	0.005	1.0	100.0
4,4'-DDD	0.005	1.0	100.0
4,4'-DDE	0.007	1.0	100.0
4,4'-DDT	0.007	1.0	100.0
Dieldrin	0.005	1.0	100.0
Endosulfan I	0.005	1.0	100.0
Endosulfan II	0.005	1.0	100.0
Endosulfan Sulfate	0.005	1.0	100.0
Endrin	0.005	1.0	100.0
Endrin Aldehyde	0.02	1.0	100.0
Endrin Ketone	0.006	1.0	100.0
Heptachlor	0.005	1.0	100.0
Heptachlor Epoxide	0.005	1.0	100.0
Methoxychlor	0.009	1.0	100.0
Chlordane	0.030	5.0	100.0
Toxaphene	0.60	100.0	2000

Table 1.2-2. Reporting Limits, and Lower and Upper Standard Range for Organochlorine Pesticides in Water by EPA Method 8080/8081 (page 2 of 2).

Parameter	Reporting Limit (ug/L)[1]	Lower Standard Range (ng/mL)	Upper Standard Range (ng/mL)
Aroclor 1016	0.13	20.0	500
Aroclor 1221	0.13	20.0	500
Aroclor 1232	0.13	20.0	500
Aroclor 1242	0.13	20.0	500
Aroclor 1248	0.13	20.0	500
Aroclor 1254	0.13	20.0	500
Aroclor 1260	0.13	20.0	500

[1] Based on the lowest standard that ESE routinely uses, taking into account the sample volume and final extract volume. The lowest standard is chosen to be within the range of 5 to 10 times the background noise of the instrument.

2.0 APPARATUS, INSTRUMENTATION AND CHEMICALS

2.1 Hardware and Glassware

2.1.1 Continuous liquid-liquid extractor.

2.1.2 Evaporative flasks [Kuderna-Danish (KD), 500-mL].

2.1.3 Snyder columns (KD, 3-ball micro- and modified micro-Snyder).

2.1.4 Concentrator tubes (KD, 25-mL graduated, with ground-glass stoppers).

2.1.5 Glass funnels (58-mm short stem).

2.1.6 Volumetric flasks (5, 10, 50 and 100 mL).

2.1.7 Volumetric pipettes (0.5- to 25-mL).

2.1.8 Pasteur pipettes (disposable).

2.1.9 Amber glass vials (9.0-mL with crimp caps).

2.1.10 Graduated cylinders (100 and 1,000 mL).

2.1.11 Hengar boiling chips (10/40 mesh; pre-extracted with methylene chloride; available from Hengar Co., Philadelphia, Penn.; Catalog No. 136-CC).

2.1.12 Glass wool (silanized).

2.1.13 Glass vials (2-mL with Teflon -lined crimp seal caps for use with automatic sampler).

2.1.14 Microsyringes (100- and 500-uL).

2.1.15 Hot water bath.

2.1.16 Analytical balance [Mettler AE160, or equivalent, with 0.0001-gram (g) sensitivity].

2.1.17 Tipit (50-mL).

2.1.18 Stainless steel spatulas.

2.1.19 0-14 pH test strips (or equivalent).

2.1.20 15-mL graduated centrifuge tubes.

2.1.21 Liquid chromatographic columns (8mm ID x 300mm).

2.1.22 Graduated pipette (1-mL disposable).

2.2 Instrumentation

A Hewlett-Packard (HP) Model 5890 gas chromatograph equipped with an electron capture detector and an HP 7672A (or 7673A) auto sampler interfaced to an HP Model 3392A (or 3393A) integrator and a computer data system.

2.2.1 Detector: electron capture, Nickel-63

2.2.2 Columns and Conditions:

2.2.2.1 Capillary

Primary:

30M x 0.25mm (0.25um film) DB-17 (50% methyl- 50% phenyl polysiloxane) capillary (Manufactured by J & W Scientific or equivalent).

Secondary:

30M x 0.25mm (0.25um film) DB-5 (95% dimethyl- 5% diphenyl polysiloxane) capillary (Manufactured by J & W Scientific or equivalent).

Head Pressure: 15 PSI (Will vary slightly with column)

Carrier: Helium; 20- to 30-centimeter-per-second (cm/sec) linear velocity (calculated).

Auxiliary: 95-percent argon/5-percent methane (P-5); 60 milliliters per minute (mL/min)

Zone Temperatures:

Injector: 270 degrees Celsius (°C)

Detector: 300°C

Oven: 50°C for 1.0 minute (min), then programmed at 50 degrees Celsius per minute (°C/min) to 150°C, then programmed at 5°C/min to 275°C and held for at least 25 min;

Injection volume: 1.0 microliter (uL) splitless, open septum purge at 45 seconds;

2.2.2.2 Megabore

Primary:

30M x 0.53mm (0.8um film) DB-608 fused silica megabore (Manufactured by J & W Scientific, or equivalent).

Secondary:

30M x 0.53mm (1.0um film) DB-1701 fused silica megabore (Manufactured by J&W Scientific or equivalent).

Flow Rate: 6 ml/min (constant flow)(will vary with column)

Carrier: Helium, Ultra Pure Carrier Grade (UPC)

Auxilliary: P-5; 60 ml/min

Zone Temperatures:

Injector: Temperature Programmed:
150°C, 40°C/min to 250°C

Detector: 300°C

Oven: Temperature Programmed: 140°C/1 min to 230°C at 9°^C/min hold for 1 min, 230°C to 260°C at 5°C/min hold for 1 min, 260°C

to 275°C at 15°C/min hold for 20 min.

Injection Volume: 1 uL on-column

2.3 Chemicals

2.3.1 Reagents

2.3.1.1 Methylene chloride (pesticide-grade).

2.3.1.2 Hexane (pesticide-grade).

2.3.1.3 Acetone (pesticide-grade).

2.3.1.4 Sodium sulfate American Chemical Society (ACS) granular, anhydrous dried at 400°C for 4 hours].

2.3.1.5 Sodium hydroxide (reagent-grade).

2.3.1.6 Sulfuric acid.

2.3.1.7 Silica gel (Woelm 60-80 mesh; 3 percent deactivated)

2.3.1.8 USAEC Standard Water: HPLC water with 100 mg/L each of added sulfate and chloride.

2.3.2 Standards:

2.3.2.1 Calibration standards, calibration check standards and spike standards should be prepared from materials traceable back to (National Institute of Standards and Technology (NIST) or U.S. Environmental Protection Agency (EPA) standard materials for purity and source.

2.3.2.2 Reference materials obtained from the EPA or NIST do not need to be characterized.

2.3.2.3 A neat material or solution purchased from a private vendor must be accompanied by a certificate of analysis.

3.0 CALIBRATION

3.1 Preparation of Instrument Calibration Standards

3.1.1 Stock Standard Solutions: All primary standards must be prepared from commercially available sources and be of certified quality. The primary standards and surrogate analytes decachlorobiphenyl (DCBP) and tetrachloro-m-xylene (TCX) will be prepared at 1 mg/mL in pesticide residue grade hexane. A small volume of acetone may be added to completely dissolve the neat standard.

3.1.1.1 Twenty-five milligrams of the neat analyte is weighed into a 25 mL volumetric flask and diluted to volume with pesticide residue grade hexane. The primary stock solution (PSS) should be prepared every twelve months or sooner if degradation is observed. Once prepared the PSS should be stored in an amber bottle with a teflon lined septum sealed cap. The solutions should be maintained at 4°C when not being used for standards preparation. ± 2°C

3.1.2 Secondary Composite Stocks(SCS): All SCS solutions are prepared by combining in a 100 mL volumetric flask 1 mL of each single component pesticide of interest and 4 mL of the surrogate stock solution and diluting to 100 mL with hexane. The nominal concentration for each analyte in the SCS is 10 ug/mL, 40 ug/mL for the surrogates. The multicomponent analytes must be diluted in separate 100 mL volumetric flasks (Aroclors 1016 and 1260 may be combined).

3.1.3 Preparation of Working Standards:

3.1.3.1 Single component pesticides and surrogates will be diluted in hexane to achieve the following concentrations:

	Single Component Concentration, ng/mL	Surrogate Concentration,ng/mL
IND1	1.0	4.0
IND2	5.0	20.0
IND3	10.0	40.0
IND4	25.0	100.0
IND5	50.0	200.0
IND6	100.0	400.0

3.1.3.2 Individual working standards are prepared by diluting 1 mL of the SCS to 100 mL with hexane to generate standard IND6. IND5 is prepared by diluting 0.5 mL of the SCS to 100 mL. Twenty-five, 10, 5, and 1 milliliters of IND6 is pipeted into separate 100 mL volumetric flasks and diluted to 100 mL to generate IND4, IND3, IND2 and IND1 respectively.

3.1.3.3 The multi-component analytes are prepared at the following concentrations:

Chlordane - 5, 10, 25, 50, 100 ng/mL

Toxaphene - 100, 200, 500, 1000, 2000 ng/mL

Aroclors - 20, 50, 100, 200, 500 ng/mL

3.2 Instrument Calibration and Analysis of Calibration Data

Daily and initial calibration prcedures are the same. The instrument should be calibrated by the following procedure at the start of each 48 hour run sequence

3.2.1 Instrument calibration: 1.0 uL is injected for each of the daily instrument calibration standards listed in section 5.3.2. The standard preparation procedures for these standards are documented in Section 3.1. The response versus the concentration of the standard injected for each component of the analyzed pesticides is regressed using a quadratic equation to obtain a working curve. The response for the sum of the individual components for each of the control PCBs, Aroclors 1260 and 1016, for the 100 ng/mL standard is plotted and a one point calibration is used to quantitate the daily control spike samples. A qualitiative check is performed for all multicomponent compounds. If a possible hit is detected, a full curve for the compound of interest will be analyzed and the sum of the responses for each component peak of the analyzed multicomponent compound versus the concentration of the standard injected is regressed using a quadratic equation to obtain a working curve. The calibration standard concentrations are outlined in Section 3.1.3.3.

3.2.2 Analysis of Calibration Data and Calibration Checks.

3.2.2.1 The curve obtained for each compound should have a correlation coefficient of $\geq$ 0.995.

3.2.2.2 One independent reference standard should be run at least weekly to verify that the calibration standards are accurate. The found concentration (from the calibration curve) for each compound in the reference sample should have a recovery (% of true value) within $\pm$ 25 % or within the criteria of the source of the reference material.

3.2.2.3 Analysis of a performance evaluation mixture (PEM), or a CCS (IND6) and an instrument blank will be analyzed at least every 12 hours and at the end of the analytical run and will be used to assess the instrument performance. The PEM sample will be used to assess inertness of the analytical system by degradation of the endrin and 4,4'-DDT to their respective degradation products.The PEM will consist of:

Lindane	10 ng/mL
alpha-BHC	10 ng/mL
beta-BHC	10 ng/mL
Endrin	50 ng/mL
4,4'-DDT	100ng/mL
TCX	20 ng/mL
DCBP	20 ng/mL

3.2.2.3.1 The combined endrin/4,4'-DDT degradation must be less than 30%. If this criterion is not met the system must be deactivated and the affected samples reanalyzed if endrin or 4,4'-DDT or their degradation products are detected in the samples.

3.2.2.4 A CCS (Continuing Calibration Standard) (IND6) or a PEM will be analyzed every 12 hours (alternating). The response for the CCS must be within $\pm$ 25 percent of the response of the same concentration as determined from the beginning-of-the-day calibrations. If this criterion is not met, the daily standard must be rerun. If the response from the second run does not meet the criteria an adequate explanation

will be provided to support the reason this situation does not affect the quality of the data reported for these samples , otherwise, a new initial calibration must be performed and affected samples must be reanalyzed.

3.2.2.5 An instrument blank will be run every 12 hours. The instrument blank will be used to assess system cleanliness. If carryover is detected in the blank, affected samples will be reanalyzed after the carryover is removed by maintenance activities. Instrument blanks can be run more often if required.

3.3 Spike Solution Preparation

3.3.1 Stock Spike Solutions(SSS): All primary standards must be prepared from commercially available sources and be of certified quality.

3.3.1.1 Stock Spike Solutions of the control analytes, listed below, are prepared at 1 mg/mL in pesticide residue grade acetone by weighing 25 mg of neat analyte into a 25 ml volumetric flask and diluting to volume with acetone.

Organochlorine Pesticide Spike	Aroclor Spike
Lindane	Aroclor 1016
Heptachlor	Aroclor 1260
Aldrin	
Dieldrin	
Endrin	
4,4'-DDT	
Endosulfan I	
alpha-Chlordane	
Methoxychlor	

3.3.1.2 Stock Spike Solutions of the surrogate analytes, decachlorobiphenyl (DCBP) and tetrachloro-m-xylene (TMX), are prepared at 1 mg/mL in pesticide residue grade acetone by weighing 25 mg of neat analyte into a 25 ml volumetric flask and diluting to volume with acetone.

Note: When the compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock spike solutions can be used if they are certified by the manufacturer or an independent source.

3.3.2 Combined Stock Spike Solutions (CSSS)

3.3.2.1 Prepare a combined stock spike solution of the pesticide control analytes by adding 2 mL of the 1 mg/mL Stock Spike Solution (SSS), for each control analyte (4 mL for Methoxychlor), to a 100 mL volumetric flask and diluting to volume with pesticide grade acetone (nominal concentration is 20 ug/mL for each analyte, 40 ug/mL for Methoxychlor).

3.3.2.2 Prepare a combined stock spike solution of surrogate analytes by adding 2 mL of the 1 mg/mL Stock Spike Solution (SSS), for each control analyte, to a 100 mL volumetric flask and diluting to volume with pesticide grade acetone (nominal concentration is 20 ug/mL for each analyte).

3.3.2.3 Prepare a combined stock spike solution of the PCB control compounds by adding 2.5 mL of the 1 mg/mL Stock Spike Solution (SSS) for each Aroclor to a 25 mL volumetric flask and diluting to volume with pesticide grade acetone (nominal concentration is 100 ug/mL for each Aroclor).

3.3.3 Working Spike Solutions:

3.3.3.1 High Spike (OCP): Prepare a working high spike solution of control spike analytes by adding 0.5 mL of the control analyte CSSS solution to a 100 mL volumetric and bringing to volume with acetone.

3.3.3.2 Low Spike (OCP): Prepare a working low spike solution of control spike analytes by adding 10 mL of the high spike solution a 100 mL volumetric and bringing to volume with acetone.

3.3.3.3 Nominal (OCP) concentrations are 100 ng/mL for each analyte in the high spike solution and 10 ng/mL for each analyte in the low spike solution. One mL of the high spike working solution will be added to 1000 mL of USAEC standard water to achieve the following high spike targets. One mL of the low spike working solution will be added to 1000 mL of USAEC standard water to achieve the following low spike targets.

3.3.3.4 High Spike (PCB): Prepare a working high spike solution of control spike analytes by adding 3 mL of the control analyte CSSS solution to a 100 mL volumetric and bringing to volume with acetone.

3.3.3.2 Low Spike (PCB): Prepare a working low spike solution of control spike analytes by adding 10 mL of the High Spike solution to 100 mL volumetric and bringing to volume with acetone.

3.3.3.3 Nominal concentrations are 3000 ng/mL for each analyte in the high spike solution and 300 ng/mL for each analyte in the low spike solution. One mL of the high spike working solution will be added to 1 liter of USAEC standard water to achieve the following high spike targets. One mL of the low spike working solution will be added to 1 liter of USAEC standard water to achieve the following low spike targets.

Analyte	Low Spike Target, ug/L	High Spike Target, ug/L
Lindane	0.010	0.100
Heptachlor	0.010	0.100
Aldrin	0.010	0.100
Dieldrin	0.010	0.100
Endrin	0.010	0.100
4,4'-DDT	0.010	0.100
Endosulfan I	0.010	0.100
alpha-Chlordane	0.010	0.100
Methoxychlor	0.020	0.200
Aroclor 1016	0.3	3.0
Aroclor 1260	0.3	3.0

3.3.3.4 Working Surrogate Spike: 5 mL of the surrogate solution (Sec. 3.3.2.2) is added to a 100 mL volumetric and brought to volume with acetone. 1.0 mL of the working surrogate spike solution is added to each environmental and QC sample prior to extraction. The target concentration of the surrogate is 200 ng/mL in the extract or 1 ug/L in the sample.

3.4 Solution Verification

3.4.1 Verification of the calibration standards is based on the analysis of daily QC spikes and of independently prepared reference standards.

3.4.2 The daily QC working spike solution will be verified prior to initial use and when samples have not been spiked and the QC are determined to be in control within the previous week.

4.0 SAMPLE HANDLING AND STORAGE

4.1 Sampling Procedure

There are no special considerations required due to the nature of pesticides. The samples need to be chilled to 4 degrees C immediately following sampling.

4.2 Storage Conditions

Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4 degrees C.

4.3 Holding Times

The holding time is 7 days from sampling to extraction and 40 days after extraction to analysis.

5.0 PROCEDURE

Daily control spike samples and environmental samples are prepared for analysis and analyzed as follows:

5.1 Extraction Procedure

5.1.1 Place 100 ml of methylene chloride into a continuous liquid-liquid extractor then add 1000 ml of the environmental sample into the continous liquid-liquid extractor.

5.1.2 Check the pH of the sample with wide-range pH paper and adjust to within the range of 6 to 8 with sodium hydroxide or sulfuric acid.

5.1.3 All samples and control samples must be fortified with surrogate compounds prior to the extraction. Each sample is fortified with 1 mL of surrogate prior to initiation of the extraction.

5.1.4 Fortify the two low spikes and two high spikes using 1 ml of the appropriate spike solution.

5.1.5 Add 350 mL of methylene chloride and a boiling chip to each boiling flask .

5.1.6 Extract the sample by applying heat, with a heating mantle for 18 hours.

5.1.7 Allow the organic layer to separate from the water phase.

5.1.8 Pass the methylene chloride extract through unwashed, baked (400°C, 4 hours) sodium sulfate into a 500-mL KD apparatus. Rinse the sodium sulfate with methylene chloride after the extract has drained.

5.1.9 Add 1 to 2 clean boiling chips to the KD apparatus and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top.

5.1.10 Place the KD apparatus on the hot water bath (60 to 65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. When the apparent volume of liquid reaches 5 mL, remove the KD apparatus and allow it to drain for at least 10 min while cooling.

5.1.11 Remove the concentrator tube, and rinse the flask and its lower joint into the

concentrator tube with about 5 mL of methylene chloride.

5.1.12 Attach a modified micro-Snyder column to the concentrator tube and partially immerse the concentrator tube in the hot water bath, which has been increased to about 80 to 85°C. When the apparent volume of the liquid reaches 2 mL, add hexane to an apparent volume of 5 mL, reduce the volume to approximately 1 mL, add hexane again, and reduce to approximately 1 mL. Remove the concentrator tube and allow it to cool for about 10 min.

5.1.13 Adjust the volume to 5.0 mL with hexane.

5.2 Optional Silica Gel Clean-up

5.2.1 Add 1.0 g of silica gel (3 percent deactivated) to a 14.6 mm Giant-Pette pipet plugged with a small piece of Pyrex glass wool in the tip. Tap the column to settle the silica and add approximately 1 cm of anhydrous sodium sulfate to the top of silica gel.

5.2.2 Transfer 2 mL of the hexane extract to the top of the silica gel using a calibrated 1-mL disposable pipette. Transfer the remaining extract to a 10 ml brown amber vial and seal with a teflon lined septum cap. Allow the extract to drain into the column.

5.2.3 Elute the column with 15 mL of 50 percent methylene chloride in hexane (v/v) collecting the extract in a graduated concentrator tube.

5.2.4 Attach a modified micro-Snyder column to the concentrator tube and partially immerse the concentrator tube in the hot water bath, which has been increased to about 80 to 85°C. When the apparent volume of the liquid reaches 2 mL, add hexane to an apparent volume of 5 mL, reduce the volume to approximately 1 mL, add hexane again, and reduce to approximately 1 mL. Remove the concentrator tube and allow it to cool for about 10 min.

5.2.5 Adjust the volume to 2 mL with hexane.

5.2.6 Transfer the cleaned-up extract to a 4.0-mL amber glass vial and cap tightly.

5.2.7 Store sample extracts at 4°C until analysis. Sample extracts must be analyzed within 40 days of sample extraction.

5.3 Instrumental Analysis

5.3.1 Perform the daily instrument calibration as described in Section 3.2.

5.3.2 Place the sample extracts in the autosampler and inject 1 uL of each sample extract on each column pair using the following procedure:

1. PEM
2. IND1
3. IND2
4. IND3
5. IND4
6. IND5
7. IND6
8. Aroclor 1016/1260 100 ng/mL
9. Aroclor 1221 100 ng/mL
10. Aroclor 1232 100 ng/mL
11. Aroclor 1242 100 ng/mL
12. Aroclor 1248 100 ng/mL
13. Aroclor 1254 100 ng/mL
14. Toxaphene 500 ng/mL
15. Tech. Chlordane 25ng/mL
16. Inst. Blank
17. Method Blank
18. Low Spike Control Sample
19. Samples.......
    Twelve Hours
    CCS (IND6)
    Inst. Blank
    High Spike Control Sample
    Samples..........
    Twelve Hours
    PEM
    Inst. Blank
    Low Spike Control Sample
    Samples.......From step 19 Repeat for up to 48 hours and ending with a CCS and a PEM

Analysis sequence of the low and high control samples:

Number of 12 Hr. Periods	Period 1	Period 2	Period 3	Period 4
4	low	high	low	high
3	low high	high	low	----
2	low high	low high	----	----
1	All	----	----	----

If certain analytes are not requested they may be excluded from the analytical sequence.

5.4 Peak Identification

5.4.1 Retention Time Windows: Retention time windows for Pesticide/PCB analysis wil be set as $\pm$0.05 min for all peaks that elute before heptachlor epoxide, $\pm$0.07 min for all compounds that elute equal to or after the retention time of heptachlor epoxide except for decachlorobiphenyl whose retention window is $\pm$0.10 min measured from the initial analysis of IND6 and the initial analysis of the multicomponent analytes. A target response that falls in the window on either column shall be considered to be tentatively identified.

5.4.2 When a compound is tentatively identified the other coulmn is examined to determine if there is a target response in the retention window for that analyte. If there is a response that falls in the retention windows on both columns the compound shall be considered identified. However the analyst's judgement will depend heavily on the interpretation of the chromatograms and the analysts (with proper documentation) will have the option of not identifying a peak due to peak shape, matrix background interference or other reasons that must be documented.

6.0 CALCULATIONS

6.1 Determine the concentration of each parameter according to the following formula:

$$Concentration(ug/L) = \frac{A\ V_t\ D}{V_s}$$

where:

A = Concentration of the parameter found in the sample extract by comparison with the appropriate quadratic calibration standard curve (micrograms per L),
Vs = Volume sample extracted (1000 mL), and
Vt = Volume of final extract (5 mL).
D = Dilution Factor

7.0 DAILY QUALITY CONTROL

7.1 Control Samples

7.1.1 Method blanks will be prepared and analyzed, at a frequency of 1 standard method blank per lot, to verify that the laboratory is not a source of sample contamination.

7.1.2 Standard spikes consisting of all control analytes as defined in Section 3.3 will be prepared by spiking into USAEC Standard Water and analyzed, at a frequency of 2 low spikes and two high spikes per sample lot, to verify laboratory performance.

7.1.3 Spikes of surrogates as defined in Section 3.4 will be spiked into all environmental and QC samples to observe the recovery effects in the environmental matrix.

7.1.4 Sample matrix spikes consisting of all control analytes as defined in Section 3.3 (Standard spikes) will be prepared, **only when requested and at the requested frequency**, by spiking the high spike solution into two separate aliquots of an actual sample. The sample to be used may be designated by the client or laboratory coordinator. The sample matrix spike will be used to verify method applicability to the sample matrix.

7.2 Control Charts

Control charts are prepared using the percent recovery data from the high level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

7.2.1 Accuracy: Two-point average percent recovery for the high level spikes within each lot, and a two-point average percent recovery for the low level spikes within each lot.

7.2.2 Precision: Two-point average difference between the high concentration spike and a two-point average difference between the low concentration spike.

7.2.3 For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken. Initial warning and control limits will be determined by USAEC using laboratory performance data.

7.2.4 Out-of-control situations to be addressed are specified in Section 8.7 of the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

7.2.5 See appendix L of U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993) for discussion of modified control limits.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993)

8.2 EPA Test Method Organochlorine Pesticides and PCBs--SW846 Method 8081. U.S. Environmental Protection Agency (EPA). EPA SW846 3rd Edition, Revision 0, November 1990.

8.3 USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Document Number 0LM01.8.

8.4 ESE SOP-ASM3243-001, Rev. 3, "The Determination of Organochlorine Pesticides and PCBs in Water and Soil Samples by Gas Chromatography (EPA METHOD 8081)".

9.0 ATTACHMENTS

9.1 Method detection limit studies.

9.2 Summary of suggested run sequences.

RUN #	TOTAL HOURS	SAMPLE HOURS	12 HR*	24 HR	36 HR	48 HR
1	1		PEM1	PEM1	PEM1	PEM1
2	2		IND1	IND1	IND1	IND1
3	3		IND2	IND2	IND2	IND2
4	4		IND3	IND3	IND3	IND3
5	5		IND4	IND4	IND4	IND4
6	6		IND5	IND5	IND5	IND5
7	7		IND6	IND6	IND6	IND6
8	8		1016/1260	1016/1260	1016/1260	1016/1260
9	9		1221	1221	1221	1221
10	10		1232	1232	1232	1232
11	11		1242	1242	1242	1242
12	12		1248	1248	1248	1248
13	13		1254	1254	1254	1254
14	14		TOXAPH.	TOXAPH.	TOXAPH.	TOXAPH.
15	15		INSTBLK1	INSTBLK1	INSTBLK1	INSTBLK1
16	**16**	**0**	**METH.BLK**	**METH.BLK**	**METH.BLK**	**METH.BLK**
17	17	1	LOCP1	LOCP1	LOCP1	LOCP1
18	18	2	LOCP2	HOCP1	HOCP1	LPCB1
19	19	3	HOCP1	LPCB1	LPCB1	SPM1OCP
20	20	4	HOCP2	HPCB2	HPCB2	SPM2OCP
21	21	5	LPCB1	SPM1OCP	SPM1OCP	SAMP1
22	22	6	LPCB2	SPM2OCP	SPM2OCP	SAMP2
23	23	7	HPCB1	SAMP1	SAMP1	SAMP3
24	24	8	HPCB2	SAMP2	SAMP2	SAMP4
25	25	9	SAMP1	SAMP3	SAMP3	SAMP5
26	26	10	SAMP2	SAMP4	SAMP4	SAMP6
27	27	11	SAMP3	SAMP5	SAMP5	SAMP7
28	**28**	**12**	**CCS1**	**CCS1**	**CCS1**	**CCS1**
29	29	13	INSTBLK2	INSTBLK2	INSTBLK2	INSTBLK2
30	30	14		LOCP2	HOCP2	HOCP2
31	31	15		HOCP2	HPCB2	HPCB2
32	32	16		LPCB2	SAMP6	SAMP8
33	33	17		HPCB2	SAMP7	SAMP9
34	34	18		SAMP6	SAMP8	SAMP10
35	35	19		SAMP7	SAMP9	SAMP11
36	36	20		SAMP8	SAMP10	SAMP12
37	37	21		SAMP9	SAMP11	SAMP13
38	38	22		SAMP10	SAMP12	SAMP14
39	39	23		SAMP11	SAMP13	SAMP15
40	**40**	**24**		**PEM2**	**PEM2**	**PEM2**
41	41	25		INSTBLK3	INSTBLK3	INSTBLK3
42	42	26		CCS2	LOCP2	LOCP2
43	43	27			LPCB2	LPCB2
44	44	28			SAMP14	SAMP16
45	45	29			SAMP15	SAMP17
46	46	30			SAMP16	SAMP18
47	47	31			SAMP17	SAMP19
48	48	32			SAMP18	SAMP20
49	49	33			SAMP19	SAMP21
50	50	34			SAMP20	SAMP22
51	51	35			SAMP21	SAMP23
52	**52**	**36**			**CCS2**	**CCS2**
53	53	37			INSTBLK4	INSTBLK4
54	54	38				HOCP2
55	55	39				HPCB2
56	56	40				SAMP24
57	57	41				SAMP25
58	58	42				SAMP26
59	59	43				SAMP27
60	60	44				SAMP28
61	61	45				SAMP29
62	62	46				SAMP30

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63	63	47	SAMP31
64	64	48	PEM3
65	65	49	INSTBLK5
66	66	50	CCS3

Assumes a 60 minute run time
LOCP1 = Low OCP Spike 1
LPCB1 = Low PCB Spike 1
INSTBLK1 = Instrument Blank 1

Standards	13	13	13	13
Control	9	9	9	9
Matrix Spike	0	2	2	2
Samples	5	11	21	31
CCS	1	2	2	3
PEM	1	2	2	3
INSTBLK	2	3	4	5
TOTAL HOURS	29	42	53	66

*12 Hour Sequence can be used only when there are 5 samples or less and there are no matrix spikes.

NOTE: If interferences in the sample matrix causes the analyst to increase the hold time between samples, the above suggested sequences will not be altered. The total analysis time for samples may, therefore, slightly exceed the 12, 24, 36, or 48 hour time limit.

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TITLE: DETERMINATION OF ORGANOCHLORINE PESTICIDES AND PCBs IN SOIL SAMPLES (SW-846 METHOD 3550/8080/8081) USAEC METHOD - CAPILLARY COLUMN PST1

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TITLE: DETERMINATION OF ORGANOCHLORINE PESTICIDES AND PCBs IN SOIL SAMPLES (SW-846 METHOD 3550/8080/8081) USAEC METHOD - CAPILLARY COLUMN PST1

1.0 SUMMARY AND APPLICATION

1.1 Summary

NOTE: THIS METHOD IS APPROVED FOR CAPILLARY COLUMN AT THE TIME OF PRINTING. WHEN THE MEGABORE MDL STUDY IS SUBMITTED AND APPROVED, THEN THIS STATEMENT WILL BE REMOVED, THE METHOD HEADER CONVERTED TO REVISION 1, AND A NEW COPY PRINTED AND DISTRIBUTED.

This Standard Operating Procedure (SOP) follows EPA SW-846 protocols with additional quality control requirements applicable for the CLASS 1P analysis as specified in the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993). The analysis procedure is based on SW-846 method 8080 AND 8081 and the sample extraction and preparation method is based on SW-846 method 3550 (Soxhlet extraction). The method determination of retention windows and spike analytes are based on the USEPA Contract Laboratory Program (CLP) Statement of Work for Organic Analysis, Document Number OLM01.8 SOW, which differs from SW-846 protocols.

CLP criteria allows for the analysis of OCP/PCB's by either capillary or megabore columns. USAEC has required the assignment of two separate method numbers for the two columns but has agreed to the interchangeable use of either method since reporting limits have been designed to be consistent for both columns and method detection limits studies for each column support the reporting limits. Analytical capacity is the major reason for allowing the interchangeable use of either method. Data in the USAEC data base and control charts will distinguish between which method was used.

A 15 g sample is continually extracted with methylene chloride using a soxhlet extractor. The methylene chloride is exchanged for hexane, then concentrated to a final volume of 10 milliliters (mL). The extract is then analyzed using a Gas Chromatograph equipped with Electron Capture Detector. Chromatographic conditions are described which permit the separation and measurement of the analytes in the hexane extract. Identification is performed using retention times, and

quantitation is performed using external standard curves.

1.2 Applicaton

1.2.1 This method is applicable to all environmental soil samples.

1.2.2 This method is applicable to the quantitative determination of the following organochlorine pesticides and PCBs in environmental soil samples listed in Table 1.2-1.

1.2.3 The reporting limit and the lower and upper standard range for this method are listed in Table 1.2-2.

1.2.4 Interferences

1.2.4.1 Interferences by phthalate esters can pose major problems in pesticide analysis. The interference can usually be minimized by preventing contact of reagents, glassware, apparatus, and samples with any plastic materials.

1.2.4.2 Solvents, reagents, glassware, and other sample processing equipment may yield chromatograms with interfering peaks. All reagents, glassware, and sample handling equipment must be demonstrated to be free from interferences which have retention times equal to those of the compounds of interest.

1.2.5 Analysis Rate

After instrument calibration, one analyst can analyze 20 samples in a 24-hour day. One analyst can perform approximately 20 extractions in an 8-hour day.

1.2.6 Health and Safety Information

The target compounds in this method are toxic. The preparation of all standards should be performed in a laboratory hood. Adequate dermal protection must be used when handling samples and standards.

Table 1.2-1. USAEC Acronyms and CAS Numbers for OCP's and PCB's (page 1 of 2).

Single Component Pesticides	Acronyms	CAS Number
Aldrin	ALDRN	309-00-2
Alpha-BHC	ABHC	319-84-6
Beta-BHC	BBHC	319-85-7
Delta-BHC	DBHC	319-86-8
Gamma-BHC (Lindane)	LIN	58-89-9
Chlordane (alpha)	ACLDAN	5103-71-9
Chlordane (gamma)	GCLDAN	5566-34-7
4,4'-DDD	PPDDD	75-54-8
4,4'-DDE	PPDDE	72-55-9
4,4'-DDT	PPDDT	50-29-3
Dieldrin	DLDRN	60-57-1
Endosulfan I	AENSLF	959-98-8
Endosulfan II	BENSLF	33212-65-9
Endosulfan Sulfate	ESFSO4	1031-07-8
Endrin	ENDRN	72-20-8
Endrin Aldehyde	ENDRNA	7421-93-4
Endrin Ketone	ENDRNK	53494-70-5
Heptachlor	HPCL	76-44-8
Heptachlor Epoxide	HPCLE	1024-57-5
Methoxychlor	MEXCLR	72-43-5

Table 1.2-1. USAEC Acronyms and CAS Numbers for OCP's and PCB's (page 2 of 2).

Multi-Component Pesticides	Acronym	CAS Number
Technical Chlordane	CLDAN	57-74-9
Toxaphene	TXPHEN	80001-35-2
Aroclor 1016	PCB016	12674-11-2
Aroclor 1221	PCB221	1104-28-2
Aroclor 1232	PCB232	11141-16-5
Aroclor 1242	PCB242	53469-21-9
Aroclor 1248	PCB248	12672-29-6
Aroclor 1254	PCB254	11097-69-1
Aroclor 1260	PCB260	11096-82-5

Table 1.2-2. Reporting Limits, and Lower and Upper Standard Range for Organochlorine Pesticides in Soil by EPA Method 8080/8081 (page 1 of 2).

Parameter	Reporting Limit (ug/g)[1]	Lower Standard Range (ng/mL)	Upper Standard Range (ng/mL)
Aldrin	0.003	1.0	100
Alpha-BHC	0.003	1.0	100
Beta-BHC	0.003	1.0	100
Delta-BHC	0.003	1.0	100
Gamma-BHC (Lindane)	0.003	1.0	100
Chlordane (alpha)	0.003	1.0	100
Chlordane (gamma)	0.003	1.0	100
4,4'-DDD	0.003	1.0	100
4,4'-DDE	0.003	1.0	100
4,4'-DDT	0.003	1.0	100
Dieldrin	0.003	1.0	100
Endosulfan I	0.003	1.0	100
Endosulfan II	0.003	1.0	100
Endosulfan Sulfate	0.003	1.0	100
Endrin	0.003	1.0	100
Endrin Aldehyde	0.022 *	1.0	100
Endrin Ketone	0.003	1.0	100
Heptachlor	0.003	1.0	100
Heptachlor Epoxide	0.003	1.0	100
Methoxychlor	0.003	1.0	100
Chlordane	0.02	5.0	100
Toxaphene	0.3	100	2000

* High reporting limit due to contamination in USAEC standard soil causing coeluting peak on DB-17 column. The DB-5 column should be used for quantitation of Endrin aldehyde in soils.

Table 1.2-2. Reporting Limits, and Lower and Upper Standard Range for Organochlorine Pesticides in Soil by EPA Method 8080/8081 (page 2 of 2).

Parameter	Reporting Limit (ug/g)[1]	Lower Standard Range (ng/mL)	Upper Standard Range (ng/mL)
Arochlor 1016	0.013	20	500
Arochlor 1221	0.013	20	500
Arochlor 1232	0.013	20	500
Arochlor 1242	0.013	20	500
Arochlor 1248	0.013	20	500
Arochlor 1254	0.013	20	500
Arochlor 1260	0.013	20	500

[1] Based on the lowest standard that ESE routinely uses, taking into account the sample volume and final extract volume. The lowest standard is chosen to be within the range of 5 to 10 times the background noise of the instrument. The solid reporting limits are expressed on a wet weight basis.

2.0 APPARATUS, INSTRUMENTATION AND CHEMICALS

2.1 Hardware and Glassware

2.1.1 Soxhlet extractor with boiling flask.

2.1.2 Evaporative flasks [Kuderna-Danish (KD), 500-mL].

2.1.3 Snyder columns (KD, 3-ball micro- and modified micro-Snyder).

2.1.4 Concentrator tubes (KD, 25-mL graduated, with ground-glass stoppers).

2.1.5 Glass funnels (58-mm short stem).

2.1.6 Volumetric flasks (5, 10, 50 and 100 mL).

2.1.7 Volumetric pipettes (0.5- to 25-mL).

2.1.8 Pasteur pipettes (disposable).

2.1.9 Amber glass vials (9.0-mL with crimp caps).

2.1.10 Graduated cylinders (100 and 1,000 mL).

2.1.11 Hengar boiling chips (10/40 mesh; pre-extracted with methylene chloride; available from Hengar Co., Philadelphia, Penn.; Catalog No. 136-CC).

2.1.12 Glass wool (silanized).

2.1.13 Glass vials (2-mL with Teflon -lined crimp seal caps for use with automatic sampler).

2.1.14 Microsyringes (100- and 500-uL).

2.1.15 Hot water bath.

2.1.16 Analytical balance [Mettler AE160, or equivalent, with 0.0001-gram (g) sensitivity].

2.1.17 Tipit (50-mL).

2.1.18 Stainless steel spatulas.

2.1.19 0-14 pH test strips (or equivalent).

2.1.20 15-mL graduated centrifuge tubes.

2.1.21 Liquid chromatographic columns (8mm ID x 300mm).

2.1.22 Graduated pipette (1-ml disposable).

2.2 Instrumentation

A Hewlett-Packard (HP) Model 5890 gas chromatograph equipped with an electron capture detector and an HP 7672A (or 7673A) auto sampler interfaced to an HP Model 3392A (or 3393A) integrator and a computer data system.

2.2.1 Detector: electron capture, Nickel-63

2.2.2 Columns and Conditions:

2.2.2.1 Capillary

Primary:

30M x 0.25mm (0.25um film) DB-17 (50% methyl- 50% phenyl polysiloxane) capillary (Manufactured by J & W Scientific or equivalent).

Secondary:

30M x 0.25mm (0.25um film) DB-5 (95% dimethyl- 5% diphenyl polysiloxane) capillary (Manufactured by J & W Scientific or equivalent).

Head Pressure: 15 PSI (Will vary slightly with column)

Carrier: Helium; 20- to 30-centimeter-per-second (cm/sec) linear velocity (calculated).

Auxiliary: 95-percent argon/5-percent methane (P-5); 60 milliliters per minute (mL/min)

Zone Temperatures:

Injector: 270 degrees Celsius (°C)

Detector: 300°C

Oven: 50°C for 1.0 minute (min), then programmed at 50 degrees Celsius per minute (°C/min) to 150°C, then programmed at 5°C/min to 275°C and held for at least 25 min;

Injection volume: 1.0 microliter (uL) splitless, open septum purge at 45 seconds;

2.2.2.2 Megabore

Primary:

30M x 0.53mm (0.8um film) DB-608 fused silica megabore (Manufactured by J & W Scientific, or equivalent).

Secondary:

30M x 0.53mm (1.0um film) DB-1701 fused silica megabore (Manufactured by J&W Scientific or equivalent).

Flow Rate: 6 ml/min (constant flow)(will vary with column)

Carrier: Helium, Ultra Pure Carrier Grade (UPC)

Auxilliary: P-5; 60 ml/min

Zone Temperatures:

Injector: Temperature Programmed:
150°C, 40°C/min to 250°C

Detector: 300°C

Oven: Temperature Programmed: 140°C/1 min to 230°C at 9°^C/min hold for 1 min, 230°C to 260°C at 5°C/min hold for 1 min, 260°C to 275°C at 15°C/min hold for 20 min.

Injection Volume: 1 uL on-column

2.3 Chemicals

2.3.1 Reagents

2.3.1.1 Methylene chloride (pesticide-grade).

2.3.1.2 Hexane (pesticide-grade).

2.3.1.3 Acetone (pesticide-grade).

2.3.1.4 Sodium sulfate American Chemical Society (ACS) granular, anhydrous dried at 400°C for 4 hours].

2.3.1.5 Sodium hydroxide (reagent-grade).

2.3.1.6 Sulfuric acid.

2.3.1.7 Silica gel (Woelm 60-80 mesh; 3 percent deactivated)

2.3.1.8 USAEC Standard Soil.

2.3.2 Standards:

2.3.2.1 Calibration standards, calibration check standards and spike standards should be prepared from materials traceable back to (National Institute of Standards and Technology (NIST) or U.S. Environmental Protection Agency (EPA) standard materials for purity and source.

2.3.2.2 Reference materials obtained from the EPA or NIST do not need to be characterized.

2.3.2.3 A neat material or solution purchased from a private vendor must be accompanied by a certificate of analysis.

3.0 CALIBRATION

3.1 Preparation of Instrument Calibration Standards

3.1.1 Stock Standard Solutions: All primary standards must be prepared from commercially available sources and be of certified quality. The primary standards and surrogate analytes decachlorobiphenyl (DCBP) and tetrachloro-m-xylene (TCX) will be prepared at 1 mg/mL in pesticide residue grade hexane. A small volume of acetone may be added to completely dissolve the neat standard.

3.1.1.1 Twenty-five milligrams of the neat analyte is weighed into a 25 mL volumetric flask and diluted to volume with pesticide residue grade hexane. The primary stock solution (PSS) should be prepared every twelve months or sooner if degradation is observed. Once prepared the PSS should be stored in an amber bottle with a teflon lined septum sealed cap. The solutions should be maintained at 4°C when not being used for standards preparation.

3.1.2 Secondary Composite Stocks(SCS): All SCS solutions are prepared by combining in a 100 mL volumetric flask 1 mL of each single component pesticide of interest and 4 mL of the surrogate stock solution and diluting to 100 mL with hexane. The nominal concentration for each analyte in the SCS is 10 ug/mL, 40 ug/mL for the surrogates. The multicomponent analytes must be diluted in separate 100 mL volumetric flasks (Aroclors 1016 and 1260 may be combined).

3.1.3 Preparation of Working Standards:

3.1.3.1 Single component pesticides and surrogates will be diluted in hexane to achieve the following concentrations:

	Single Component Concentration, ng/mL	Surrogate Concentration, ng/mL
IND1	1.0	4.0
IND2	5.0	20.0
IND3	10.0	40.0
IND4	25.0	100.0
IND5	50.0	200.0
IND6	100.0	400.0

3.1.3.2 Individual working standards are prepared by diluting 1 mL of the SCS to 100 mL with hexane to generate standard IND6. IND5 is

prepared by diluting 0.5 mL of the SCS to 100 mL. Twenty-five, 10, 5, and 1 milliliters of IND6 is pipeted into separate 100 mL volumetric flasks and diluted to 100 mL to generate IND4, IND3, IND2 and IND1 respectively.

3.1.3.3 The multi-component analytes are prepared at the following concentrations:

Chlordane - 5, 10, 25, 50, 100 ng/mL

Toxaphene - 100, 200, 500, 1000, 2000 ng/mL

Aroclors - 20, 50, 100, 200, 500 ng/mL

3.2 Instrument Calibration and Analysis of Calibration Data

Daily and initial calibration prcedures are the same. The instrument should be calibrated by the following procedure at the start of each 48 hour run sequence.

3.2.1 Instrument calibration: 1.0 uL is injected for each of the daily instrument calibration standards listed in section 5.3.2. The standard preparation procedures for these standards are documented in Section 3.1. The response versus the concentration of the standard injected for each component of the analyzed pesticides is regressed using a quadratic equation to obtain a working curve. The response for the sum of the individual components for each of the control PCBs, Aroclors 1260 and 1016, for the 100 ng/mL standard is plotted and a one point calibration is used to quantitate the daily control spike samples. A qualitiative check is performed for all multicomponent compounds. If a possible hit is detected, a full curve for the compound of interest will be analyzed and the sum of the responses for each component peak of the analyzed multicomponent compound versus the concentration of the standard injected is regressed using a quadratic equation to obtain a working curve. The calibration standard concentrations are outlined in Section 3.1.3.3.

3.2.2 Analysis of Calibration Data and Calibration Checks.

3.2.2.1 The curve obtained for each compound should have a correlation coefficient of 0.995 of greater.

3.2.2.2 One independent reference standard should be run at least weekly to verify that the calibration standards are accurate. The found concentration (from the calibration curve) for each compound in the reference sample should have a recovery (% of true value) within ± 25 % or within the criteria of the source of the reference material.

3.2.2.3 Analysis of a performance evaluation mixture (PEM), or a CCS (IND6) and an instrument blank will be analyzed at least every 12 hours and at the end of the analytical run and will be used to assess the instrument performance. The PEM sample will be used to assess inertness of the analytical system by degradation of the endrin and 4,4'-DDT to their respective degradation products.The PEM will consist of:

Lindane	10 ng/mL
alpha-BHC	10 ng/mL
beta-BHC	10 ng/mL
Endrin	50 ng/mL
4,4'-DDT	100ng/mL
TCX	20 ng/mL
DCBP	20 ng/mL

3.2.2.3.1 The combined endrin/4,4'-DDT degradation must be less than 30%. If this criterion is not met the system must be deactivated and the affected samples reanalyzed if endrin or 4,4'-DDT or their degradation products are detected in the samples.

3.2.2.4 A CCS (Continuing Calibration Standard) (IND6) or a PEM will be analyzed every 12 hours (alternating). The response for the CCS must be within ± 25 percent of the response of the same concentration as determined from the beginning-of-the-day calibrations. If this criterion is not met, the daily standard must be rerun. If the response from the second run does not meet the criteria an adequate explanation will be provided to support the reason this situation does not affect the quality of the data reported for these samples or a new initial calibration must be performed and affected samples must be reanalyzed.

3.2.2.5 An instrument blank will be run every 12 hours. The instrument blank will be used to assess system cleanliness. If carryover is detected in the blank, affected samples will be reanalyzed after the carryover is removed by maintenance activities. Instrument blanks can

be run more often if required.

3.3 Spike Solution Preparation

3.3.1 Stock Spike Solutions(SSS): All primary standards must be prepared from commercially available sources and be of certified quality.

3.3.1.1 Stock Spike Solutions of the control analytes, listed below, are prepared at 1 mg/mL in pesticide residue grade acetone by weighing 25 mg of neat analyte into a 25 ml volumetric flask and diluting to volume with acetone.

Organochlorine Pesticide Spike	Aroclor Spike
Lindane	Aroclor 1016
Heptachlor	Aroclor 1260
Aldrin	
Dieldrin	
Endrin	
4,4'-DDT	
Endosulfan I	
alpha-Chlordane	
Methoxychlor	

3.3.1.2 Stock Spike Solutions of the surrogate analytes, decachlorobiphenyl (DCBP) and tetrachloro-m-xylene (TCX), are prepared at 1 mg/mL in pesticide residue grade acetone by weighing 25 mg of neat analyte into a 25 ml volumetric flask and diluting to volume with acetone.

Note: When the compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock spike solutions can be used if they are certified by the manufacturer or an independent source.

3.3.2 Combined Stock Spike Solutions (CSSS)

3.3.2.1 Prepare a combined stock spike solution of the pesticide control analytes by adding 2 mL of the 1 mg/mL Stock Spike Solution (SSS), for each control analyte , to a 100 mL volumetric flask and diluting to volume with pesticide grade acetone (nominal concentration is 20 ug/mL for each analyte).

3.3.2.2 Prepare a combined stock spike solution of surrogate analytes by adding 2 mL of the 1 mg/mL Stock Spike Solution (SSS), for each control analyte, to a 100 mL volumetric flask and diluting to volume with pesticide grade acetone (nominal concentration is 20 ug/mL for each analyte).

3.3.2.3 Prepare a combined stock spike solution of the PCB control compounds by adding 4 mL of the 1 mg/mL Stock Spike Solution (SSS) for each Aroclor to a 100 mL volumetric flask and diluting to volume with pesticide grade acetone (nominal concentration is 40 ug/mL for each Aroclor).

3.3.3 Working Spike Solutions:

3.3.3.1 High Spike (OCP): Prepare a working high spike solution of control spike analytes by adding 4.0 mL of the control analyte CSSS solution to a 100 mL volumetric and bringing to volume with acetone.

3.3.3.2 Low Spike (OCP): Prepare a working low spike solution of control spike analytes by adding 0.5 mL of the control analyte CSSS solution to a 100 mL volumetric and bringing to volume with acetone.

3.3.3.3 Nominal OCP concentrations are 800 ng/mL for each analyte in the high spike solution and 100 ng/mL for each analyte in the low spike solution. One mL of the high spike working solution will be added to 15 grams of USAEC standard soil to achieve the following high spike targets. One mL of the low spike working solution will be added to 15 grams of USAEC standard soil to achieve the following low spike targets.

3.3.3.4 High Spike (PCB): Prepare a working high spike solution of control spike analytes by adding 10 mL of the control analyte CSSS solution to a 100 mL volumetric and bringing to volume with acetone.

3.3.3.2 Low Spike (PCB): Prepare a working low spike solution of control spike analytes by adding 1 mL of the control analyte CSSS to a 100 mL volumetric and bringing to volume with acetone.

3.3.3.3 Nominal concentrations are 4000 ng/mL for each analyte in the high spike solution and 400 ng/mL for each analyte in the low spike solution. One mL of the high spike working solution will be added to 15 grams of USAEC standard soil to achieve the following high spike

targets. One mL of the low spike working solution will be added to 15 grams of USAEC standard soil to achieve the following low spike targets.

Analyte	Low Spike Target, ug/g	High Spike Target, ug/g
Lindane	0.0067	0.053
Heptachlor	0.0067	0.053
Aldrin	0.0067	0.053
Dieldrin	0.0067	0.053
Endrin	0.0067	0.053
4,4'-DDT	0.0067	0.053
Endosulfan I	0.0067	0.053
alpha-Chlordane	0.0067	0.053
Methoxychlor	0.0067	0.053
Aroclor 1016	0.026	0.26
Aroclor 1260	0.026	0.26

3.3.3.4 Surrogate Spike: Five mL of the surrogate solution (Sec. 3.3.2.2) is added to a 100 mL volumetric and brought to volume with acetone. One mL of the working surrogate spike is added to each environmental and QC sample prior to extraction. The target concentration of the surrogate is 100 ng/mL in the extract or 0.0667 ug/g on the soil.

3.3.4 Stock spike solutions must be replaced after one year, or sooner if comparison with the spike verification indicates a problem.

3.3.5 Working spike solutions must be replaced after 6 months, or sooner if comparison with the spike verification indicates a problem.

3.4 Solution Verification

3.4.1 Verification of the calibration standards is based on the analysis of daily QC spikes and of independently prepared reference standards.

3.4.2 The daily QC working spike solution will be verified prior to initial use and when samples have not been spiked and the QC are determined to be in

control within the previous week.

4.0 SAMPLE HANDLING AND STORAGE

4.1 Sampling Procedure

There are no special considerations required due to the nature of pesticides. The samples need to be chilled to 4 degrees C immediately following sampling.

4.2 Storage Conditions

Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4 degrees C.

4.3 Holding Times

The holding time is 7 days from sampling to extraction and 40 days after extraction to analysis.

5.0 PROCEDURE

Daily control spike samples and environmental samples are prepared for analysis and analyzed as follows:

5.1 Extraction Procedure

5.1.1 Place 15 g of the environmental sample or AEC standard soil into a beaker.

5.1.2 Add baked Na_2SO_4 to dry the sample.

5.1.3 Transfer the sample to a clean extraction thimble and place in a soxhlet extractor. Spike the two low and two high control spikes with 1 mL of the appropriate spike solution.

5.1.4 Add 1 mL of surrogate spike solution and allow to sit for 1 hour.

5.1.5 Add boiling chips and 350 mL of methylene chloride to each of the boiling flasks.

5.1.6 Extract the sample by applying heat, with a heating mantle for 16 hours.

5.1.7 Transfer the methylene chloride to a 500 mL KD apparatus by pouring the sample through a funnel filled with Na_2SO_4.

5.1.8 Add 1 to 2 clean boiling chips to the KD apparatus and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top.

5.1.9 Place the KD apparatus on the hot water bath (60 to 65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. When the apparent volume of liquid reaches 5 mL, remove the KD apparatus and allow it to drain for at least 10 min while cooling.

5.1.10 Remove the concentrator tube, and rinse the flask and its lower joint into the concentrator tube with about 5 mL of methylene chloride.

5.1.11 Attach a modified micro-Snyder column to the concentrator tube and partially immerse the concentrator tube in the hot water bath, which has been increased to about 80 to 85°C. When the apparent volume of the liquid reaches 2 mL, add hexane to an apparent volume of 5 mL, reduce the volume to approximately 1 mL, add hexane again, and reduce to approximately 1 mL. Remove the concentrator tube and allow it to cool for about 10 min.

5.1.12 Adjust the volume to 10.0 mL with hexane.

5.2 Silica Gel Clean-up

5.2.1 Add 3.0 g of silica gel (3 percent deactivated) to an 8 mm inner diameter by 150 mm glass column plugged with a small piece of Pyrex glass wool in the tip. Tap the column to settle the silica and add approximately 1 cm of anhydrous sodium sulfate to the top of silica gel.

5.2.2 Transfer 2 mL of the hexane extract to the top of the silica gel using a calibrated 1-mL disposable pipette. Transfer the remaining extract to a 10 mL brown amber vial and seal with a teflon lined septum cap. Allow the extract to drain into the column.

5.2.3 Elute the column with 35 mL of 50 percent methylene chloride in hexane (v/v) collecting the extract in a graduated concentrator tube.

5.2.4 Attach a modified micro-Snyder column to the concentrator tube and partially immerse the concentrator tube in the hot water bath, which has been increased to about 80 to 85°C. When the apparent volume of the liquid reaches 2 mL, add hexane to an apparent volume of 5 mL, reduce the volume to approximately 1 mL, add hexane again, and reduce to approximately 1 mL. Remove the concentrator tube and allow it to cool for about 10 min.

5.2.5 Adjust the volume to 2 mL with hexane.

5.2.6 Transfer the cleaned-up extract to a 4.0-mL amber glass vial and cap tightly.

5.2.7 Store sample extracts at 4°C until analysis. Sample extracts must be analyzed within 40 days of sample extraction.

5.3 Instrumental Analysis

5.3.1 Perform the daily instrument calibration as described in Section 3.2.

5.3.2 Place the sample extracts in the autosampler and inject 1 uL of each sample extract on each column pair using the following procedure:

1. PEM
2. IND1
3. IND2
4. IND3
5. IND4
6. IND5
7. IND6
8. Aroclor 1016/1260 100 ng/mL
9. Aroclor 1221 100 ng/mL
10. Aroclor 1232 100 ng/mL
11. Aroclor 1242 100 ng/mL
12. Aroclor 1248 100 ng/mL
13. Aroclor 1254 100 ng/mL
14. Toxaphene 500 ng/mL
15. Tech. Chlordane 25ng/mL
16. Inst. Blank
17. Method Blank
18. Low Spike Control Sample OCP
19. Low Spike Control Sample PCB
20. Samples.......
    Twelve Hours
    CCS (IND6)
    Inst. Blank
    High Spike Control Sample (OCP)
    High Spike Control Sample (PCB)
    Samples..........
    Twelve Hours
    PEM
    Inst. Blank
    Low Spike Control Sample (OCP)
    Low Spike Control Sample (PCB)
    Samples.......From step 20 Repeat for up to 48 hours and ending with a CCS and a PEM

Analysis sequence of the low and high control samples:

Number of 12 Hr. Periods	Period 1	Period 2	Period 3	Period 4
4	low	high	low	high
3	low high	high	low	----
2	low high	low high	----	----
1	All	----	----	----

If certain analytes are not requested they may be excluded from the analytical sequence.

5.4 Peak Identification

5.4.1 Retention Time Windows: Retention time windows for Pesticide/PCB analysis wil be set as ±0.05 min for all peaks that elute before heptachlor epoxide, ±0.07 min for all compounds that elute equal to or after the retention time of heptachlor epoxide except for decachlorobiphenyl whose retention window is ±0.10 min measured from the initial analysis of IND6 and the initial analysis of the multicomponent analytes. A target response that falls in the window on either column shall be considered to be tentatively identified.

5.4.2 When a compound is tentatively identified the other coulmn is examined to determine if there is a target response in the retention window for that analyte. If there is a response that falls in the retention windows on both columns the compound shall be considered identified. However the analyst's judgement will depend heavily on the interpretation of the chromatograms and the analysts (with proper documentation) will have the option of not identifying a peak due to peak shape, matrix background interference or other reasons that must be documented.

6.0 CALCULATIONS

6.1 Determine the concentration of each parameter according to the following formula:

$$Concentration(ug/g) = \frac{A\ V_t}{W_s}$$

where:

A = Concentration of the parameter found in the sample extract by comparison with the appropriate quadratic calibration standard curve (micrograms per mL),
Ws = Weight sample extracted (15 grams), and
Vt = Volume of final extract (10 mL).

Moisture content of the soil is sent to the USAEC data management system along with the ug/g wet weight concentration and any dilution factor.

7.0 DAILY QUALITY CONTROL

7.1 Control Samples

7.1.1 Method blanks will be prepared and analyzed, at a frequency of 1 standard method blank per lot, to verify that the laboratory is not a source of sample contamination.

7.1.2 Standard spikes consisting of all control analytes as defined in Section 3.3 will be prepared by spiking into USAEC Standard Soil and analyzed, at a frequency of 2 low spikes and two high spikes per sample lot, to verify laboratory performance.

7.1.3 Spikes of surrogates as defined in Section 3.4 will be spiked into <u>all</u> environmental and QC samples to observe the recovery effects in the environmental matrix.

7.1.4 Sample matrix spikes consisting of all OCP control analytes as defined in Section 3.3 (Standard spikes) will be prepared, **only when requested and at the requested frequency**, by spiking the high spike solution into two separate aliquots of an actual sample. The sample to be used may be designated by the client or laboratory coordinator. The sample matrix spike will be used to verify method applicability to the sample matrix.

7.2 Control Charts

Control charts are prepared using the percent recovery data from the high level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

7.2.1 Accuracy: Two-point average percent recovery for the high level spikes within each lot, and a two-point average percent recovery for the low level spikes within each lot.

7.2.2 Precision: Two-point average difference between the high concentration spike and a two-point average difference between the low concentration spike.

7.2.3 For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken. Initial warning and control limits will be determined by USAEC using laboratory performance data.

7.2.4 Out-of-control situations to be addressed are specified in Section 8.7 of the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

7.2.5 See appendix L of U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993) for discussion of modified control limits.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993)

8.2 EPA Test Method Organochlorine Pesticides and PCBs--SW846 Method 8081. U.S. Environmental Protection Agency (EPA). EPA SW846 3rd Edition, Revision 0, November 1990.

8.3 USEPA Contract Laboratory Program Statement of Work for Organic Analysis, Document Number 0LM01.8.

8.4 ESE SOP-ASM3243-001, Rev. 3, "The Determination of Organochlorine Pesticides and PCBs in Water and Soil Samples by Gas Chromatography (EPA METHOD 8081)".

9.0 ATTACHMENTS

9.1 Method detection limit studies.

9.2 Summary of suggested run sequences.

RUN #	TOTAL HOURS	SAMPLE HOURS	12 HR*	24 HR	36 HR	48 HR
1	1		PEM1	PEM1	PEM1	PEM1
2	2		IND1	IND1	IND1	IND1
3	3		IND2	IND2	IND2	IND2
4	4		IND3	IND3	IND3	IND3
5	5		IND4	IND4	IND4	IND4
6	6		IND5	IND5	IND5	IND5
7	7		IND6	IND6	IND6	IND6
8	8		1016/1260	1016/1260	1016/1260	1016/1260
9	9		1221	1221	1221	1221
10	10		1232	1232	1232	1232
11	11		1242	1242	1242	1242
12	12		1248	1248	1248	1248
13	13		1254	1254	1254	1254
14	14		TOXAPH.	TOXAPH.	TOXAPH.	TOXAPH.
15	15		INSTBLK1	INSTBLK1	INSTBLK1	INSTBLK1
16	**16**	**0**	**METH.BLK**	**METH.BLK**	**METH.BLK**	**METH.BLK**
17	17	1	LOCP1	LOCP1	LOCP1	LOCP1
18	18	2	LOCP2	HOCP1	HOCP1	LPCB1
19	19	3	HOCP1	LPCB1	LPCB1	SPM1OCP
20	20	4	HOCP2	HPCB2	HPCB2	SPM2OCP
21	21	5	LPCB1	SPM1OCP	SPM1OCP	SAMP1
22	22	6	LPCB2	SPM2OCP	SPM2OCP	SAMP2
23	23	7	HPCB1	SAMP1	SAMP1	SAMP3
24	24	8	HPCB2	SAMP2	SAMP2	SAMP4
25	25	9	SAMP1	SAMP3	SAMP3	SAMP5
26	26	10	SAMP2	SAMP4	SAMP4	SAMP6
27	27	11	SAMP3	SAMP5	SAMP5	SAMP7
28	**28**	**12**	**CCS1**	**CCS1**	**CCS1**	**CCS1**
29	29	13	INSTBLK2	INSTBLK2	INSTBLK2	INSTBLK2
30	30	14		LOCP2	HOCP2	HOCP2
31	31	15		HOCP2	HPCB2	HPCB2
32	32	16		LPCB2	SAMP6	SAMP8
33	33	17		HPCB2	SAMP7	SAMP9
34	34	18		SAMP6	SAMP8	SAMP10
35	35	19		SAMP7	SAMP9	SAMP11
36	36	20		SAMP8	SAMP10	SAMP12
37	37	21		SAMP9	SAMP11	SAMP13
38	38	22		SAMP10	SAMP12	SAMP14
39	39	23		SAMP11	SAMP13	SAMP15
40	**40**	**24**		**PEM2**	**PEM2**	**PEM2**
41	41	25		INSTBLK3	INSTBLK3	INSTBLK3
42	42	26		CCS2	LOCP2	LOCP2
43	43	27			LPCB2	LPCB2
44	44	28			SAMP14	SAMP16
45	45	29			SAMP15	SAMP17
46	46	30			SAMP16	SAMP18
47	47	31			SAMP17	SAMP19
48	48	32			SAMP18	SAMP20
49	49	33			SAMP19	SAMP21
50	50	34			SAMP20	SAMP22
51	51	35			SAMP21	SAMP23
52	**52**	**36**			CCS2	CCS2
53	53	37			INSTBLK4	INSTBLK4
54	54	38				HOCP2
55	55	39				HPCB2
56	56	40				SAMP24
57	57	41				SAMP25
58	58	42				SAMP26
59	59	43				SAMP27
60	60	44				SAMP28
61	61	45				SAMP29
62	62	46				SAMP30
63	63	47				SAMP31
64	64	48				**PEM3**
65	65	49				INSTBLK5
66	66	50				CCS3

Assumes a 60 minute run time
LOCP1 = Low OCP Spike 1
LPCB1 = Low PCB Spike 1
INSTBLK1 = Instrument Blank 1

Standards	13	13	13	13
Control	9	9	9	9
Matrix Spike	0	2	2	2
Samples	5	11	21	31
CCS	1	2	2	3
PEM	1	2	2	3
INSTBLK	2	3	4	5
TOTAL HOURS	29	42	53	66

*12 Hour Sequence can be used only when there are 5 samples or less and there are no matrix spikes.

NOTE: If interferences in the sample matrix causes the analyst to increase the hold time between samples, the above suggested sequences will not be altered. The total analysis time for samples may, therefore, slightly exceed the 12, 24, 36, or 48 hour time limit.

Environmental Science & Engineering, Inc.
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Gainesville, Florida

TITLE: **DETERMINATION OF TOTAL PETROLEUM (FUEL) HYDROCARBONS IN ENVIRONMENTAL WATER SAMPLES BY GAS CHROMATOGRAPHY (SW-846 METHOD 8015 MODIFIED)**
USAEC METHOD - TPH1 - WATER

TABLE OF CONTENTS

TITLE: DETERMINATION OF TOTAL PETROLEUM (FUEL) HYDROCARBONS IN ENVIRONMENTAL WATER SAMPLES BY GAS CHROMATOGRAPHY (SW-846 METHOD 8015 MODIFIED)
USAEC METHOD - TPH1 - WATER

1.0 SUMMARY AND APPLICATION

1.1 Summary

1.1.1 This Standard Operating Procedure (SOP) follows EPA SW-846 protocols with additional quality control requirements applicable for the CLASS 1 analysis as specified in the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993). The SOP describes the analysis of petroleum fuels, gasoline range fuels thru heavy diesel fuels, in environmental water samples. This method is based on the EPA reference methods SW846 Method 8015 and the California LUFT method for fuels analysis.

1.1.2 A measured volume of sample (100 mL) is extracted with 5 ml carbon disulfide by tumbling the extraction bottle for 1 hour. The carbon disulfide extract is then analyzed by gas chromatography with flame ionization detection. Chromatographic conditions are described which permit the separation and measurement of the analytes in the carbon disulfide extract. Identification is performed using pattern recognition and retention envelopes. Quantitation is performed using external standard curves.

1.1.3 Method deviations: The reference method uses a purge and trap and solvent extraction methods to determine analytes by GC/FID. The analysis described herein uses the solvent extraction method to analyze for both the gasoline range and diesel range organics in the same run.

1.2 Application

1.2.1 This method is applicable to all environmental water samples.

1.2.2 This method is applicable to the quantitative determination of solvent extractable petroleum fuels in environmental water samples:

Analyte	USAEC Acronym	CAS Registry Number
Gasoline	GAS	86290-81-5
Diesel Fuels	DIESEL	68476-34-6
Aviation Gasoline		
Jet Fuels (JP Series)		
Crude Oil up to n-C30		

1.2.3 The reporting limit and the lower and upper standard range for this method are listed in the following tables.

Reporting Limits, and Lower and Upper Standard Range for Total Petroleum Hydrocarbons in Water by EPA Method 8015 modified.

COMPOUND	LOWER STANDARD (ug/mL)	UPPER STANDARD (ug/mL)	REPORTING LIMIT[1] (mg/L)
GAS	8	4000	0.4
DIESEL (Includes JP series fuels)	8	4000	0.4
PENTACOSANE (SURROGATE)	1	125	NA

Based on the lowest standard that ESE routinely uses, taking into account the sample volume and final extract volume. The lowest standard is chosen to be within the range of 5 to 10 times the background noise of the instrument.

1.2.4 Interferences

1.2.4.1 Interferences in the trace level determination of substances can originate from numerous sources. The FID detector is not selective and will detect many volatile organic compounds. Any organic compound that is solvent extractable and elutes in

the elution envelopes of the fuels that will respond to the FID is a potential interference.

1.2.4.2 Contamination can arise from the matrix in which the sample is found, the cleanliness of glassware and the care in which the sample is handled by laboratory personnel. Solvents, reagents, glassware, and other sample processing equipment may yield chromatograms with interfering peaks. All reagents, glassware, and sample handling equipment must be demonstrated to be free from interferences which have retention times equal to those of the compounds of interest.

1.2.4.3 Samples can also be contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent handling can serve as a check on such contamination.

1.2.4.4 This method will detect most hydrocarbons that are partitioned and extracted into carbon disulfide.

1.2.4.5 "Fresh" fuels exhibit characteristic chromatographic patterns that can be readily identified if there is no significant weathering due to evaporation, dissolution or microbial degradation. Interferences due to non-petroleum related hydrocarbons (eg. PCBs) can result in a positive interference that can be difficult to discern due to petroleum's complex chromatographic patterns. Only analysts experienced in the analysis of petroleum hydrocarbons should perform this method.

1.2.5 Analysis Rate

After instrument calibration, one analyst can analyze 20 samples in a 24-hour day. One analyst can perform approximately 20 extractions in an 8-hour day.

1.2.6 Health and Safety Information

Carbon disulfide is highly toxic and extremely FLAMMABLE. All open containers, vials, etc., must be handled in a fume hood. The hood must not contain any heat sources, e.g., functioning hot plates.

2.0 APPARATUS, INSTRUMENTATION AND CHEMICALS

2.1 Hardware and Glassware

2.1.1 100 mL amber Boston round bottles with teflon lined septum screw caps.

2.1.2 Volumetric flasks (5, 10, 50 and 100 mL).

2.1.3 Volumetric pipettes (0.5- to 25-mL).

2.1.4 Pasteur pipettes (disposable).

2.1.5 Amber glass vials (9.0-mL with crimp caps).

2.1.6 Graduated cylinders (250 mL).

2.1.7 Glass vials (2-mL with Teflon -lined crimp seal caps for use with automatic sampler).

2.1.8 Microsyringes (100 and 500 uL).

2.1.9 Analytical balance [Mettler AE160, or equivalent, with 0.0001-gram (g) sensitivity].

2.2 Instrumentation

A Hewlett-Packard (HP) Model 5890 gas chromatograph equipped with a flame ionization detector and an HP 7672A (or 7673A) auto sampler interfaced to an HP Model 3392A (or 3393A) integrator and a computer data system.

2.2.1 Detector: Flame Ionization Detector (FID)

2.2.2 Column and Conditions:

Column description:
30-meter (m) x 0.32-millimeter (mm) internal diameter DB-1 fused-silica capillary column with 1.0-micron (u) film thickness.

Head Pressure: 15 PSI (Will vary slightly with column)

Carrier: Helium; 20- to 30-centimeter-per-second (cm/sec) linear velocity (calculated).
Auxiliary: Nitrogen, 30 milliliters per minute (mL/min)

Zone Temperatures:

Injector: 250 degrees Celsius (°C)

Detector: 300°C

Oven: 45°C for 1.0 minute (min), then programmed at 5 degrees Celsius per minute (°C/min) to 70°C, then held for 5 min; then at 10°C/min to 280°C and held for 10 min.

Injection volume: 2.0 microliter (uL) splitless, open septum purge at 45 seconds;

2.3 Chemicals

2.3.1 Reagents

2.3.1.1 Carbon Disulfide (pesticide-grade, Benzene free).

2.3.1.2 Acetone (pesticide-grade).

2.3.2 Standards:

2.3.2.1 Target Fuels (preferably from study location)

2.3.2.2 Pentacosane (nC25), Surrogate Standard

2.3.2.3 USAEC Standard Water

3.0 STANDARD PREPARATION

3.1 Calibration Standards

3.1.1 Stock Standard Solutions: All primary standards are technical grade fuels and considered to be 100% pure for the purposes of this procedure unless otherwise specified by the supplier i.e., vendor supplied solution. Where possible source material should be used for calibration. If during the analysis of samples a fuel type other than gasoline or diesel is detected, the samples will be reanalyzed after calibration with a similar fuel type. The fuel standards will be prepared as follows.

3.1.1.2 A stock standard is prepared gravimetrically in carbon disulfide. Weigh 500 mg of gasoline and diesel fuel into a 25mL volumetric flask and dilute to volume with carbon disulfide. The concentration of this stock solution is 20,000 ug/mL.

3.1.1.3 A Surrogate Stock is prepared by weighing 63 mg nC25 into a 25mL volumetric flask and diluting to volume with CS_2. The final concentration is 2520 mg/mL.

3.1.2 Four mL of the standard stock, and 1 mL of the surrogate stock are diluted to 20 mL with CS_2 in a 20 mL volumetric flask. This is standard A. Two mL each of the standard and surrogate stock are diluted to 50 mL with CS_2 in a volumetric flask. This is standard B.

* Similarity, 0.5 mL of each stock is diluted to 25 mL with CS_2. This is standard C.

* Five mL of standard B is diluted to 20 mL with CS_2. This is standard D.

* One mL of standard B is diluted to 20 mL. This is standard E.

* Five mL of standard E is diluted to 25 mL. This is standard F.

COMPOUND	NOMINAL CALIBRATION STANDARD CONCENTRATIONS (ug/mL)					
	STD A	STD B	STD C	STD D	STD E	STD F
GAS	4000	800	400	200	40	8
DIESEL	4000	800	400	200	40	8
PENTACOSANE (SURROGATE)	125	100	50	25	5	1

3.2 Spike Solution Preparation

3.2.1 Stock Spike Solutions(SSS): Due to the nature of fuel sources the control spike solution shall be made from the same technical material as the calibration standards.

3.2.1.1 If the type of fuel to be expected in the samples is known, then that type of fuel should be used in the preparation of spike solutions. If the type of fuel is not known, then a diesel and gasoline stock spike solution should be prepared in acetone.

3.2.1.2 A stock spike solution is prepared by weighing 500 mg of gasoline and diesel fuel into 25 ml volumetric flask and dilute to volume with acetone. The nominal concentration of analyte in this stock is 20,000 mg/mL.

3.2.1.3 Water Spike Solution: A working water spike solution is prepared by diluting 5 mL of the spike solution (3.2.1.2) into a 50 mL volumetric flask and diluting to volume with acetone. Nominal concentration is 2000 ug/mL.

3.2.2 Surrogate Spike Solution: The surrogate spike solution is prepared by weighing 125 milligrams of nC25 into a 50 mL volumetric flask, dissolving in 5 mL CS_2, and diluting to volume with acetone. 100 uL will be added to each sample prior to analysis.

3.2.3 The low spike in standard water is spiked with 50 uL of the working spike solution and the two high spikes in standard water are spiked with 400 uL spike solution. (Matrix spikes and matrix spike duplicates are not required by the USAEC, however if the project requires these spikes the MS/MSD spikes will be spiked with 400 ul of the spike solution.)

COMPOUND	WATER SPIKE SOLUTION CONC. (ug/mL)	SPIKE SOLUTION VOLUME (uL)		TARGET CONCENTRATION IN SAMPLE (mg/L)	
		LOW SPIKE	HIGH SPIKE	LOW SPIKE	HIGH SPIKE
GAS & DIESEL	2000	50	400	1000	8000
PENTACOSANE (SURROGATE)	2500	100	100	2500	2500

3.3 Solution Verification

3.3.1 Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards.

3.3.2 The daily QC working spike solution will be verified prior to initial use and when samples have not been spiked and QC determined to be in control within the previous week.

4.0 INSTRUMENT CALIBRATION

4.1 Initial and daily instrument calibration, 2.0 uL is injected for each of the daily instrument calibration standards. The response versus the concentration of the standard injected for each component is regressed using a quadratic equation to obtain a working curve.

4.2 The curve obtained for each compound should have a correlation coefficient of $\geq$ 0.995.

4.3 One independent reference standard should be run at least weekly to verify that the calibration standards are accurate. The found concentration (from the calibration curve) for each compound in the reference sample should have a recovery (% of true value) within $\pm$ 25 % or within the criteria of the source of the reference material.

4.4 Continuing calibration standards (CCS) will be analyzed every 10 samples to demonstrate system stability. STD A will be used as the CCS. The response of the CCS must be within $\pm$ 25% of the initial response. If the response fails to meet this criteria the CCS must be reanalyzed. If this CCS fails criteria all samples run since the last acceptable CCS must be reanalyzed or documentation provided by the analyst as to why the sample data should be acceptable.

5.0 SAMPLE HANDLING AND STORAGE

5.1 Sample Collection

5.1.1 Samples must be collected in accordance with sampling procedures for volatile samples. Samples must be collected with no headspace and minimal contact with the atmosphere.

5.1.2 The samples need to be chilled to 4 degrees C immediately following sampling.

5.2 Sample Containers

Sampling containers used are 100 mL amber Boston Round Bottles with teflon lined septum sealed screw caps.

5.3 Storage Conditions

Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4 degrees C.

5.4 Holding Times

The holding time is 14 days from sampling to analysis.

revised 10/13/93 ACT

6.0 PROCEDURE

Daily control spike samples and environmental samples are prepared for analysis and analyzed as follows:

6.1 Extraction Procedure

6.1.1 Remove 10 mL of sample from the middle of the sample and discard.

6.1.2 Immediately spike the sample with 100 uL of the surrogate spike and add 5 mL carbon disulfide and cap.

6.1.3 Prepare standard spikes in USAEC standard water as follows:

6.1.3.1 The low spike sample (approximately 100 mL of standard water) is spiked with 50 uL of the working spike solution

6.1.3.2 The two high spike samples (each approximately 100 mL of standard water) are spiked with 400 uL spike solution.

6.1.3.3 Matrix spikes and matrix spike duplicates are not required by the USAEC, however **if the project requires** these spikes, the MS/MSD spikes will be spiked with 400 uL of the spike solution.

6.1.4 The samples are tumbled for one hour to complete the extraction.

6.1.5 The carbon disulfide layer is removed for GC analysis using a transfer pipet.

6.1.6 Store sample extracts at 4°C until analysis. Sample extracts must be analyzed within 7 days of sample extraction.

6.1.7 The sample bottle contents are discarded and the bottle is refilled with water. The water is then transferred to a graduated cylinder to determine the volume of the original sample. The volume is calculated to be 10 mL less than the volume of water measured, to take into account the 10 mL of sample removed in the first step of the extraction procedure (Section 6.1.1). revised 10/13/93

6.2 Instrumental Analysis

6.2.1 Perform the daily instrument calibration using the calibration standards previously described.

6.2.2 Place the sample extracts in the autosampler and inject 2 uL of each sample extract on each column pair using the following procedure:

1. STD F
2. STD E
3. STD D
4. STD C
5. STD B
6. STD A
7. Instrument Blank
8. METHOD BLANK
9. LOW SPIKE
10. HIGH SPIKE 1
11. HIGH SPIKE 2

12. - 16. SAMPLES

17. STD A

10 SAMPLES FOLLOWED BY STD A
RUN MUST END WITH STD A

6.3 Peak Identification

Retention Envelopes: Petroleum fuels contain hundreds of compounds that elute in a pattern characteristic of the fuel. A fuel will exhibit a pattern that elutes over a time frame known as the boiling range or envelope. Both the characteristic pattern and envelope will be used to identify a fuel type. If the fuel type cannot be identified, the sample will be quantified using the responses from the most closely eluting boiling envelope.

7.0 CALCULATIONS

7.1 Peak areas will be summed over the retention envelope and regressed against a standard curve to determine the concentrate of analyte in the extract. The concentration of each parameter is calculated according to the following formula:

$$Concentration(ug/L) = \frac{A\ V_t\ D}{V_s}$$

where:

A = Concentration of the parameter found in the sample extract by comparison with the appropriate quadratic calibration standard curve (micrograms per L),
Vs = Volume of sample extracted (100 mL), and
Vt = Volume of final extract (5 mL).
D = Dilution Factor

8.0 DAILY QUALITY CONTROL

8.1 Control Samples

8.1.1 Method blanks will be prepared and analyzed, at a frequency of 1 standard method blank per lot, to verify that the laboratory is not a source of sample contamination.

8.1.2 Standard spikes consisting of all control analytes as defined in Section 3.2.2 will be prepared by spiking into USAEC Standard Water and analyzed, at a frequency of 1 low spike and two high spikes per sample lot, to verify laboratory performance.

8.1.3 Spikes of surrogates as defined in Section 3.2.3 will be spiked into all environmental and QC samples to observe the recovery effects in the environmental matrix.

8.1.4 Sample matrix spikes consisting of all control analytes as defined in Section 3.2.2 (Standard spikes) will be prepared, **only when requested and at the requested frequency**, by spiking the standard spike solution into two separate aliquots of an actual sample. The sample to be used may be designated by the client or laboratory coordinator. The sample matrix spike will be used to verify method applicability to the sample matrix.

8.2 Control Charts

Control charts are prepared using the percent recovery data from the high level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

8.2.1 Accuracy: Two-point average percent recovery for the high level spikes within each lot, and a three-point moving average percent recovery for the low level spikes within each lot.

8.2.2 Precision: Two-point average difference between the high concentration spike and a three-point moving average difference between the low concentration spikes.

8.2.3 For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken. Initial warning and control limits will be determined by USAEC using laboratory performance data.

8.2.4 Out-of-control situations to be addressed are specified in Section 8.7 of U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

8.2.5 See appendix L of U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993) for discussion of modified control limits.

9.0 REFERENCES

9.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993)

9.2 EPA Method 8015 -- Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.3 ESE SOP-ASM3243-005, Rev. 0, "The Determination of Total Petroleum (Fuel) Hydrocarbons in Water and Soil Samples by Gas Chromatography (Modified EPA 8015)".

10.0 ATTACHMENTS

10.1 Method detection limit studies.

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **DETERMINATION OF TOTAL PETROLEUM (FUEL) HYDROCARBONS IN ENVIRONMENTAL SOIL SAMPLES BY GAS CHROMATOGRAPHY (SW-846 METHOD 8015 MODIFIED)**
USAEC METHOD - TPH1 - SOIL

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TITLE: DETERMINATION OF TOTAL PETROLEUM (FUEL) HYDROCARBONS IN ENVIRONMENTAL SOIL SAMPLES BY GAS CHROMATOGRAPHY (SW-846 METHOD 8015 MODIFIED) USAEC METHOD - TPH1 - SOIL

1.0 SUMMARY AND APPLICATION

1.1 Summary

1.1.1 This Standard Operating Procedure (SOP) follows EPA SW-846 protocols with additional quality control requirements applicable for the CLASS 1 analysis as specified in the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993). The SOP describes the analysis of petroleum fuels, gasoline range fuels thru heavy diesel fuels, in environmental soil samples. This method is based on the EPA reference methods SW846 Method 8015 and the California LUFT method for fuels analysis.

1.1.2 A measured volume of sample (10 grams) is extracted with 10 ml carbon disulfide by tumbling the extraction bottle for 1 hour.

1.2.3 The carbon disulfide extract is then analyzed by gas chromatography with flame ionization detection. Chromatographic conditions are described which permit the separation and measurement of the analytes in the carbon disulfide (CS_2) extract. Identification is performed using pattern recognition and retention envelopes. Quantitation is performed using external standard curves.

1.2 Applicaton

1.2.1 This method is applicable to all environmental soil samples.

1.2.2 This method is applicable to the quantitative determination of solvent extractable petroleum fuels in environmental soil samples:

Analyte	USAEC Acronym	CAS Registry Number
Gasoline	GAS	86290-81-5
Diesel Fuels	DIESEL	68476-34-6
Aviation Gasoline		
Jet Fuels (JP Series)		
Crude Oil up to n-C30		

1.2.3 The reporting limit and the lower and upper standard range for this method are listed in the following tables.

Reporting Limits, and Lower and Upper Standard Range for Total Petroleum Hydrocarbons in Soil by EPA Method 8015 modified.

COMPOUND	LOWER STANDARD (ug/mL)	UPPER STANDARD (ug/mL)	REPORTING LIMIT1 (ug/g)
GAS	8	4000	8
DIESEL (Includes JP series fuels)	8	4000	8
PENTACOSANE (SURROGATE)	1	125	NA

Based on the lowest standard that ESE routinely uses, taking into account the sample volume and final extract volume. The lowest standard is chosen to be within the range of 5 to 10 times the background noise of the instrument. The solid reporting limits are expressed on a wet weight basis.

1.2.4 Interferences

1.2.4.1 Interferences in the trace level determination of substances can originate from numerous sources. The FID detector is not selective and will detect many volatile organic compounds. Any organic compound that is solvent extractable and elutes in the elution envelopes of the fuels that will respond to the FID is a potential interference.

1.2.4.2 Contamination can arise from the matrix in which the sample is found, the cleanliness of glassware and the care in which the sample is handled by laboratory personnel. Solvents, reagents, glassware, and other sample processing equipment may yield chromatograms with interfering peaks. All reagents, glassware, and sample handling equipment must be demonstrated to be free from interferences which have retention times equal to those of the compounds of interest.

1.2.4.3 Samples can also be contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent handling can serve as a check on such contamination.

1.2.4.4 This method will detect most hydrocarbons that are partitioned and extracted into carbon disulfide.

1.2.4.5 "Fresh" fuels exhibit characteristic chromatographic patterns that can be readily identified if there is no significant weathering due to evaporation, dissolution or microbial degradation. Interferences due to non-petroleum related hydrocarbons (eg. PCBs) can result in a positive interference that can be difficult to discern due to petroleum's complex chromatographic patterns. Only analysts experienced in the analysis of petroleum hydrocarbons should perform this method.

1.2.5 Analysis Rate

After instrument calibration, one analyst can analyze 20 samples in a 24-hour day. One analyst can perform approximately 20 extractions in an 8-hour day.

1.2.6 Health and Safety Information

Carbon disulfide is highly toxic and extremely FLAMMABLE. All open containers, vials, etc., must be handled in a fume hood. The hood must not contain any heat sources, e.g., functioning hot plates.

2.0 APPARATUS, INSTRUMENTATION AND CHEMICALS

2.1 Hardware and Glassware

2.1.1 40 ml amber VOA vials with teflon lined septum screw caps.

2.1.2 Volumetric flasks (5, 10, 50 and 100 mL).

2.1.3 Volumetric pipettes (0.5- to 25-mL).

2.1.4 Pasteur pipettes (disposable).

2.1.5 Amber glass vials (9.0-mL with crimp caps).

2.1.6 Graduated cylinders (250 mL).

2.1.7 Glass vials (2-mL with Teflon -lined crimp seal caps for use with automatic sampler).

2.1.8 Microsyringes (10, 100 and 500 uL).

2.1.9 Analytical balance [Mettler AE160, or equivalent, with 0.0001-gram (g) sensitivity].

2.2 Instrumentation

A Hewlett-Packard (HP) Model 5890 gas chromatograph equipped with a flame ionization detector and an HP 7672A (or 7673A) auto sampler interfaced to an HP Model 3392A (or 3393A) integrator and a computer data system.

2.2.1 Detector: Flame Ionization Detector (FID)

2.2.2 Column and Conditions:

Column description:
30-meter (m) x 0.32-millimeter (mm) internal diameter DB-1 fused-silica capillary column with 1.0-micron (u) film thickness.

Head Pressure: 15 PSI (Will vary slightly with column)

Carrier: Helium; 20- to 30-centimeter-per-second (cm/sec) linear velocity (calculated).

Auxiliary: Nitrogen, 30 milliliters per minute (mL/min)

Zone Temperatures:

Injector: 250 degrees Celsius (oC)

Detector: 300oC

Oven: 45oC for 1.0 minute (min), then programmed at 5 degrees Celsius per minute (°C/min) to 70°C, then held for 5 min; then at 10°C/min to 280° and held for 10 min.

Injection volume: 2.0 microliter (uL) splitless, open septum purge at 45 seconds;

2.3 Chemicals

2.3.1 Reagents

2.3.1.1 Carbon Disulfide (pesticide-grade, Benzene free).

2.3.1.2 Acetone (pesticide-grade).

2.3.2 Standards:

2.3.2.1 Target Fuels (preferrably from study location)

2.3.2.2 Pentacosane (nC25), Surrogate Standard

2.3.2.3 USAEC Standard Soil.

3.0 STANDARD PREPARATION

3.1 Calibration Standards

3.1.1 Stock Standard Solutions: All primary standards are technical grade fuels and considered to be 100% pure for the purposes of this procedure unless otherwise specified by the supplier i.e., vendor supplied solution. Where possible source material should be used for calibration. If during the analysis of samples a fuel type other than gasoline or diesel is detected, the samples will be reanalyzed after calibration with a similar fuel type. The fuel standards will be prepared as follows.

3.1.1.2 A stock standard is prepared gravimetrically in carbon disulfide. Weigh 500 mg of gasoline and diesel fuel into a 25ml volumetric flask and dilute to volume with carbon disulfide. The concentration of this stock solution is 20,000 ug/ml.

3.1.1.3 A surrogate stock is prepared by weighing 62.5mg nC25 into a 25mL volumetric flask and diluting to volumn with CS_2. The final concentration is 2500 mg/mL.

3.1.2 Four mL of the standard stock, and 1mL of the surrogate stock are diluted to 20mL with CS_2 in a 20mL volumetric flask. This is standard A. Two mL each of the standard and surrogate stock are diluted to 50mL with CS_2 in a volumetric flask. This is standard B.

- Similarly, 0.5mL of each stock is diluted to 25mL with CS_2. This is standard C.
- Five mL of standard B are diluted to 20mL with CS_2. This is standard D.
- One mL of standard B is diluted to 20mL. This is standard E.
- Five mL of standard E are diluted to 25mL. This is standard F.

COMPOUND	NOMINAL CALIBRATION STANDARD CONCENTRATIONS (ug/mL)					
	STD A	STD B	STD C	STD D	STD E	STD F
GAS	4000	800	400	200	40	8
DIESEL	4000	800	400	200	40	8
PENTACOSANE (SURROGATE)	125	100	50	25	5	1

3.2 Spike Solution Preparation

3.2.1 Stock Spike Solutions(SSS): Due to the nature of fuel sources the control spike solution shall be made from the same technical material as the calibration standards.

3.2.1.1 If the type of fuel to be expected in the samples is known, then that type of fuel should be used in the preparation of spike solutions. If the type of fuel is not known, then a diesel and gasoline stock spike solution should be prepared in acetone.

3.2.1.2 A high spike solution is prepared by weighing 400 mg of gasoline and diesel fuel into 25mL volumetric flask and dilute to volume with acetone. The nominal concentration of analytes in this solution is 16,000 mg/ml.

3.2.1.3 A low spike solution is prepared by pipetting 5mL of high spike solution into a 50mL volumetric flask and diluting to volume with acetone. The nominal concentration of analytes is this solution is 2000 mg/mL.

Surrogate Spike Solution: The surrogate spike solution is prepared by weighing 125 milligrams of nC25 into a 50 ml volumetric flask, dissolving in 5mL CS_2, and diluting to volume with acetone. 200 uL will be added to each sample prior to analysis.

COMPOUND	SPIKE SOLUTION CONC. (mg/mL)	SPIKE SOLUTION VOLUME (uL)		TARGET CONCENTRATION (ug/g)	
		LOW	HIGH	LOW	HIGH
GAS & DIESEL	16,000	-	100	-	160
GAS & DIESEL	1,600	100	-	16	-
PENTACOSANE (SURROGATE)	2,500	200		50	

3.3 Solution Verification

3.3.1 Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards.

3.3.2 The daily QC working spike solution will be verified prior to initial use and when samples have not been spiked and QC determined to be in control within the previous week.

4.0 INSTRUMENT CALIBRATION

4.1 Initial and daily instrument calibration, 2.0 uL is injected for each of the daily instrument calibration standards. The response versus the concentration of the standard injected for each component is regressed using a quadratic equation to obtain a working curve.

4.2 The curve obtained for each compound should have a correlation coefficient of ≥ 0.995.

4.3 One independent reference standard should be run at least weekly to verify that the calibration standards are accurate. The found concentration (from the calibration curve) for each compound in the reference sample should have a

recovery (% of true value) within ± 25 % or within the criteria of the source of the reference material.

4.4 Continuing calibration standards (CCS) will be analyzed every 10 samples to demonstrate system stability. STD A will be used as the CCS. The response of the CCS must be within ± 25% of the initial response. If the response fails to meet this criteria the CCS must be reanalyzed. If this CCS fails criteria all samples run since the last acceptable CCS must be reanalyzed or documentation provided by the analyst as to why the sample data should be acceptable.

5.0 SAMPLE HANDLING AND STORAGE

5.1 Sample Collection

5.1.1 Samples must be collected in accordance with sampling procedures for volatile samples. Samples must be collected with no headspace and minimal contact with the atmosphere.

5.1.2 The samples need to be chilled to 4 degrees C immediately following sampling.

5.2 Sample Containers

Sampling containers used are 40 ml amber VOA vials with teflon lined septum sealed screw caps.

5.3 Storage Conditions

Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4 degrees C.

5.4 Holding Times

The holding time is 14 days from sampling to analysis.

6.0 PROCEDURE

Daily control spike samples and environmental samples are prepared for analysis and analyzed as follows:

6.1 Extraction Procedure

6.1.1 Weigh 10 g of the environmental sample into a 40 ml VOA vial.

6.1.2 Immediately spike the sample with 200 ul of the surrogate spike and add 10 ml carbon disulfide and cap.

6.1.3 Prepare standard spikes in USAEC standard soil as follows:

6.1.3.1 The low spike in standard soil is spiked with 100 ul of the working low spike solution.

6.1.3.2 The two high spikes in standard soil are spiked with 100 ul of the working high spike solution.

6.1.3.3 Matrix spikes and matrix spike duplicates are not required by the USAEC, however **if the project requires** these spikes, the MS/MSD spikes will be spiked with 100 ul of the working high spike solution.

6.1.4 The samples are tumbled for one hour to complete the extraction.

6.1.5 The carbon disulfide layer is removed for GC analysis using a transfer pipet.

6.1.6 Store sample extracts at 4°C until analysis. Sample extracts must be analyzed within 7 days of sample extraction.

6.2 Instrumental Analysis

6.2.1 Perform the daily instrument calibration using the calibration standards previously described.

6.2.2 Place the sample extracts in the autosampler and inject 2 uL of each sample extract on each column pair using the following procedure:

1. STD F
2. STD E
3. STD D
4. STD C
5. STD B
6. STD A
7. Instrument Blank
8. METHOD BLANK
9. LOW SPIKE
10. HIGH SPIKE 1
11. HIGH SPIKE 2

12. - 16. SAMPLES

17. STD A

10 SAMPLES FOLLOWED BY STD A

RUN MUST END WITH STD A

6.3 Peak Identification

Retention Envelopes: Petroleum fuels contain hundreds of compounds that elute in a pattern characteristic of the fuel. A fuel will exhibit a pattern that elutes over a time frame known as the boiling range or envelope. Both the characteristic pattern and envelope will be used to identify a fuel type. If the fuel type cannot be identified, the sample will be quanitified using the responses from the most closely eluting boiling envelope.

7.0 CALCULATIONS

7.1 Peak areas will be summed over the retention envelope and regressed against a standard curve to determine the concentrate of analyte in the extract. The concentration of each parameter is calculated according to the following formula:

$$Concentration(ug/g) = \frac{A\ V_t\ D}{W_s}$$

where:

A = Concentration of the parameter found in the sample extract by comparison with the appropriate quadratic calibration standard curve (micrograms per mL),
Ms = Mass of sample extracted (10 g), and
Vt = Volume of final extract (10 mL).
D = Dilution Factor

8.0 DAILY QUALITY CONTROL

8.1 Control Samples

8.1.1 Method blanks will be prepared and analyzed, at a frequency of 1 standard method blank per lot, to verify that the laboratory is not a source of sample contamination.

8.1.2 Standard spikes consisting of all control analytes as defined in Section 3.2.2 will be prepared by spiking into USAEC Standard Soil and analyzed, at a frequency of 1 low spike and two high spikes per sample lot, to verify laboratory performance.

8.1.3 Spikes of surrogates as defined in Section 3.2.3 will be spiked into all environmental and QC samples to observe the recovery effects in the environmental matrix.

8.1.4 Sample matrix spikes consisting of all control analytes as defined in Section 3.2.2 (Standard spikes) will be prepared, **only when requested and at the**

requested frequency, by spiking the standard spike solution into two separate aliquots of an actual sample. The sample to be used may be designated by the client or laboratory coordinator. The sample matrix spike will be used to verify method applicability to the sample matrix.

8.2 Control Charts

Control charts are prepared using the percent recovery data from the high level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

8.2.1 Accuracy: Two-point average percent recovery for the high level spikes within each lot, and a three-point moving average percent recovery for the low level spikes within each lot.

8.2.2 Precision: Two-point average difference between the high concentration spike and a three-point moving average difference between the low concentration spikes.

8.2.3 For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken. Initial warning and control limits will be determined by USAEC using laboratory performance data.

8.2.4 Out-of-control situations to be addressed are specified in Section 8.7 of U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

8.2.5 See appendix L of U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993) for discussion of modified control limits.

9.0 REFERENCES

9.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993)

9.2 EPA Method 8015 -- Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.3 ESE SOP-ASM3243-005, Rev. 0, "The Determination of Total Petroleum (Fuel) Hydrocarbons in Water and Soil Samples by Gas Chromatography (Modified EPA 8015)".

10.0 ATTACHMENTS

10.1 Method detection limit studies.

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **GAS CHROMATOGRAPHIC ANALYSIS OF CHLORINATED HERBICIDES IN ENVIRONMENTAL WATER SAMPLES (METHOD SW-846 8150)**
USAEC METHOD - HBG1 - WATER

TABLE OF CONTENTS

TITLE: **GAS CHROMATOGRAPHIC ANALYSIS OF CHLORINATED HERBICIDES IN ENVIRONMENTAL WATER SAMPLES (METHOD SW-846 8150)**
USAEC METHOD - <u>HBG1</u> - WATER

1.0 SUMMARY AND APPLICATION

1.1 SUMMARY

1.1.1 This Standard Operating Procedure (SOP) follows EPA SW-846 protocols with additional quality control requirements applicable for the CLASS 1 analysis as specified in the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993). The analysis procedure is based on SW-846 method 8150.

1.1.2 The esters are hydrolyzed with potassium hydroxide and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and conerted to their methyl esters using diazomethane as the derivatizing agent. The excess reagent is removed.

1.1.3 The esters are determined by analyzing a 2 uL volume of extract. A temperature program is used to separate the analytes which are detected with an Electron Capture Detector (ECD). The results are reported as the acid equivalents.

1.2 APPLICATION

1.2.1 This SOP may be used to determine the following chlorinated acid herbicides by gas chromatography (GC).

Compound Name	Cas No.[a]	USAEC ACRONYM
2,4-D	94-75-7	24D
2,4-DB	94-82-6	24DB
2,4,5-T	93-76-5	245T
2,4,5-TP	93-72-1	245TP
Dalapon	75-99-0	DALA
Dicamba	1918-00-9	DCAMBA
Dichlorprop	120-36-5	DICP
Dinoseb	88-85-7	DINO
MCPA	94-74-6	MCPA
MCPP	93-65-2	MCPP
2,4 Dichlorophenyl-acetic acid (surrogate)	19719-28-9	DCAA

[a] Chemical Abstract Services Registry Number

1.2.2 The sensitivity of this method usually depends on the level of interferences rather than on instrumental limitations.

1.2.3 This SOP describes analytical conditions for a second gas chromatographic column that can be used to confirm the analysis made by the primary column.

1.2.4 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

1.2.5 Alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

1.2.6 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

1.2.7 Reporting limits for Herbicides in water are as follows:

Compound Name	Reporting Limit (ug/L)	Calibration Std Range (ng/mL) Low	High
2,4-D	0.1	5	100
2,4-DB	0.1	5	100
2,4,5-T	0.1	5	100
2,4,5-TP	0.1	5	100
Dalapon	0.1	5	100
Dicamba	0.1	5	100
Dichlorprop	0.1	5	100
Dinoseb	0.1	5	100
MCPA	3.0	200	1000
MCPP	3.0	200	1000

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2.0 APPARATUS, CHEMICALS AND INSTRUMENTATION

2.1 APPARATUS

2.1.1 Extraction

2.1.1.1 Erlenmeyer flasks: 250-mL and 500-mL Pyrex, with 24/40 ground-glass joint.

2.1.1.3 Beaker: 500-mL

2.1.1.4 Diazomethane generator: Assemble from two 20 x 150-mm test tubes, two neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Attachment I. The procedure for use of this type of generator is given in Section 7.3.3.

2.1.1.6 Separatory funnel: 2-L, 125-mL, and 60-mL.

2.1.1.7 Drying funnel: 75-mm long stem funnel (Kimax 2895075 or equivalent)

2.1.1.8 Kuderna-Danish (K-D) apparatus:

2.1.1.8.1 Concentrator tube: 25-mL, graduated (SSI 57076-180 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

2.1.1.8.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

2.1.1.8.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

2.1.1.8.4 Snyder column: Modified micro (SSI S7064-020 or equivalent).

2.1.1.9 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

2.1.1.10 Water bath: Heated, with concentric ring cover, capable of temperature control ($\pm$5° C). The bath should be used in a hood.

2.1.1.11 Wrist shaker: Burrell Model 75 or equivalent.

2.1.1.12 Glass wool: Pyrex, acid washed.

2.1.1.13 Glass rod.

2.1.2 Analysis

2.1.2.1 1 mL clear vials

2.1.2.2 Seals

2.1.2.3 9" Pasteur pipets

2.1.2.4 Crimper

2.1.2.5 Volumetric flasks - 25, 50, 100 mLs

2.1.2.6 Volumetric pipets - various sizes ranging from 0.5 to 20.0 mLs.

2.1.2.7 Amber bottles - 25 and 50 mL.

2.1.2.8 Micropipets - 50, 100 and 200 uL.

2.1.2.9 Analytical balance

2.1.2.10 Spatula

2.2 CHEMICALS

2.2.1 Extraction

2.2.1.1 Reagent water: Reagent water is defined as a water in which an interferant is not observed at the method detection limit of each parameter of interest.

2.2.1.2 Sulfuric acid solution:

2.2.1.2.1 (1:1) (v/v) - slowly add 50-mL H_2SO_4 (sp. gr. 1.84) to 50-mL of reagent water.

2.2.1.2.2 (1:3) (v/v) - slowly add 25-mL H_2SO_4 (sp. gr. 1.84) to 75-mL of reagent water.

2.2.1.3 Hydrochloric acid: (ACS), (1:9) (v/v) - add one volume of concentrated HCl to 9 volumes of reagent water.

2.2.1.4 Potassium hydroxide solution: 37% aqueous solution (w/v). Dissolve 37 g ACS grade potassium hydroxide pellets in reagent water and dilute to 100 mL.

2.2.1.5 Carbitol: (Diethylene glycol monoethyl ether): (ACS), available from Aldrich Chemical Co.

2.2.1.6 Solvents:

2.2.1.6.1 Acetone, methanol, and hexane (pesticide quality or equivalent).

2.2.1.6.2 Diethyl ether: Pesticide quality or equivalent. Must be free of peroxides, as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers).

Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethanol preservative must be added to each liter of ether.

2.2.1.7 Sodium sulfate: (ACS) granular, acidified, anhydrous. Heat treat in a shallow tray at 400° C for a minimum of 4 hr to remove phthalates and other interfering organic substances. Acidify by slurring 100 g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH of the mixture. It must be below a pH of 4. Store at 130°C.

2.2.1.8 N-Methyl-N-nitroso-p-toluenesulfonamide (Diazald): (ACS) available from Aldrich Chemical Co.

2.2.1.9 Silicic acid: chromatographic grade, nominal 100 mesh. Store at 130°C.

2.2.1.10 USAEC Standard Water

2.2.2 Analysis

2.2.2.1 Solvents

2.2.2.1.1 Methanol - Pesticide grade.

2.2.2.1.2 MTBE (methyl tert-butyl ether) - Pesticide grade.

2.2.2.1.3 Hexane - Pesticide grade

2.2.2.2 Stock Standard solutions - available from commercial vendors.

2.2.2.3 Neat - available from ChemServe or equivalent, as 99.9% pure. Chemicals of a purity 96% or less must be corrected for purity.

2.2.2.4 Solutions - available from Crescent or equivalent, as 1 mg/mL.

2.2.2.5 Stock Surrogate - 2,4-Dichlorophenyl acetic acid, 99.9%, available from Aldrich or equivalent

2.3 INSTRUMENTATION (GAS CHROMATOGRAPH)

2.3.1 Hewlett Packard 5890 Gas Chromatograph or equivalent equipped with dual Ni-63 ECD's, dual auto injectors, and capable of temperature programming is used. The GC must be accommodate two dissimilar columns. A computerized data system (HP3359) is used to collect chromatographic data.

2.3.2 Columns

2.3.2.1 Primary: DB-17 30 meter x 0.25 mm fused silica capillary column with 0.25 um film

2.3.2.2 Secondary: DB-5 30 meter x 0.25 mm fused silica capillary column with 0.25 um film

2.3.3.3 Gas Chromatographic conditions:

Injector temperature: 250° C

Detector temperature: 300° C

Column temperature ramp: 50° C/1 min to 150° C at 20°C/min, hold for 2 mins; 150°C to 200°C @ 2°C/min, hold for 0 mins; 200°C to 280°C @ 50° C/min, hold for 11 min.

Program specified is typically used. However, the temperature program may need modification to avoid interferences. This would depend upon matrix interferences. **ANY MODIFICATION MUST BE CLEARLY DOCUMENTED.**

Gases: Carrier Gas - Helium, ultra pure carrier, flow of 1 to 2 mL per minute.

Make up Gas - 5% Methane/Argon, flow of 40 to 50 mL per minute.

3.0 PREPARATION OF STANDARDS AND CALIBRATION

3.1 CALIBRATION STANDARDS

3.1.1 Stock Standard solutions - Stock standard solutions are prepared from pure standard materials.

3.1.1.1 Prepare stock standard solutions by accurately weighing 25 mg of the pure acids into a 25 mL volumetric flask. Dissolve and bring to volume in MTBE. Final concentration will be, nominally, 1 mg/mL (1000 ug/ml).

3.1.1.2 Five milliliters of each of the stock standard solutions (25mL of MCPP and MCPA) is derivatized by bubbling diazomethane in the solution as described below:

3.1.1.2.1 Assemble the diazomethane generator (ATTACHMENT I) in a hood.

3.1.1.2.1 Add 20 mL (2 inches or same height as Tube 2) of ethyl ether to Tube 1. Add 5 mL of ethyl ether, 5 mL of carbitol®, 7.5 mL of 37% aqueous KOH, and 1g diazald to Tube 2. Immediately place the exit tube into the concentrator tube containing the stock standard solution. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the first stock solution for 1 minute. Immediately remove first stock solution, replace disposable pipette tip and continue to the next solution. Diazomethane reaction mixture can be used to esterify about 3-4 samples. When samples stop turning yellow add about 2 or 3 scoops of Diazald to tube 2 and about 4 or 5 more samples can be esterified before emptying and rinsing tubes.

3.1.1.3 Transfer the stock standard solution into an amber bottle with a teflon lined screw cap. Store at 4° C and protect from light.

3.1.1.4 Stock Standard solutions must be replace after 1 year, or sooner, if comparison with check standards indicates a problem.

3.1.2 Intermediate Stock solutions

3.1.2.1 Intermediate Stock A - Pipet 1 mL of each stock standard solution into a 100 mL volumetric flask. Pipet 2 mLs of the surrogate stock standard solution (DCAA) (Section 3.1.5) and dilute with hexane to volume in a 50 ml volumetric flask (use 20 mLs of MCPP and MCPA). Final concentration will be 20 ug/mL (10,000 ng/ml) nominal (200 ug/mL for MCPP and MCPA and 20 ug/mL for DCAA).

3.1.2.2 Intermediate Stock B - Pipet 10 mL of Intermediate Stock A (3.1.2.1) into a 100 mL volumetric flask and dilute to volume with hexane. Final concentration will be 1000 ng/ml nominal (20,000 ng/mL for MCPP and MCPA and 2000 ng/mL for DCAA).

3.1.3 Working Standards - Seven calibration standards for each parameter of interest prepared through dilution of the secondary stock with hexane. They are prepared in 100 mL volumetric flasks by adding the volumes of standards as specifed below to achieve the following nominal concentrations:

				NOMINAL CONCENTRATIONS		
To Prepare	Std Used	Volume Used (mL)	Dilute to (mL)	MCPA/MCPP (ng/mL)	All Others (ng/mL)	DCAA (Surr.) (ng/mL)
STD G	Int.Stock B	0.1	50	40	2	4
STD F	Int.Stock B	0.2	50	80	4	8
STD E	Int.Stock B	0.5	50	200	10	20
STD D	Int.Stock B	1	50	400	20	40
STD C	Int.Stock B	2.5	50	1000	50	100
STD B	Int.Stock B	4	50	1600	80	160
STD A	Int.Stock B	5	50	2000	100	200

Working standards must be prepared every six months, or sooner, if comparison with a check standard indicates a problem.

3.1.4 Quality Control Check Standards (ICV) - a quality control check standard is prepared by diluting a commercially prepared composite mix of the methyl esters to a nominal concentration equivalent to STD A. in hexane.

3.1.5 Surrogate Standards - The analyst should monitor the performance of the extraction, cleanup (when used), analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard spike sample, sample matrix spike and reagent water blank with 2,4-Dichlorophenyl acetic acid (DCAA). Prepare a stock standard solution by accurately weighing 25 mg of the DCAA into a 25 mL volumetric flask. Dissolve and bring to volume in

methanol. Final concentration will be, nominally, 1 mg/mL (1000 ug/ml).

3.1.5.1 Secondary Stock Surrogate solution - Pipet 1 mL of primary stock surrogate solution into a 100 mL volumetric flask and fill to volume with methanol. Final concentration is 10 ug/mL (10,000 ng/mL) 2,4-Dichlorophenyl acetic acid.

3.1.5.2 Working solution - Pipet 5.0 mLs of the secondary stock surrogate solution into a 50 mL volumetric flask and fill to volume with methanol. Final concentration 1,000 ng/mL. A 1 mL aliquot must be spiked into all samples and QC samples.

3.1.6 Spike Solutions

3.1.6.1 Working Spike solution - A working spike solution should be made from a different source than the Stock Standard solution. If it is not possible to find another source, then use the same source, but from a different lot. Pipet 2 mL of each stock standard solution into a 100 mL volumetric flask. Dilute to volume with methanol. Final concentration will be 20 ug/ml (20,000 ng/mL) nominal. Spike Analytes are as follows:

2,4-D
2,4-DB
2,4,5-T
2,4,5-TP
Dichlorprop
Dicamba

3.1.6.2 High Spike Solution - A high spike solution is prepared by adding 4.0 mL of the Working Spike solution to a 100 mL volumetric flask. Bring to volume with methanol. The nominal concentration for each analyte is 800 ng/mL (or 800 ug/L).

3.1.6.3 Low Spike solution - A low spike solution is prepared by adding 1.0 mL of the Working Spike solution to a 100 mL volumetric flask. Bring to volume with methanol. The nominal concentration for each analyte is 200 ng/mL (or 200 ug/L).

Spiking levels in 1 liter of USAEC water are as follows:

Compound Name	Spike Level (ug/L) Low	High
2,4-D	0.2	0.8
2,4-DB	0.2	0.8
2,4,5-T	0.2	0.8
2,4,5-TP	0.2	0.8
Dichloroprop	0.2	0.8
Dicamba	0.2	0.8

3.2 INSTRUMENT CALIBRATION (INITIAL AND DAILY)

3.2.1 Set-up the GC according to the analytical conditions specified in Section 2.3.3.3 and load the samples onto the autosampler.

3.2.2 Use the external calibration technique to calibrate the GC system.

3.2.3 Establish retention times for all analytes and for both columns used for analysis.

3.2.4 Continuing Calibration Check Standard (CCS) - A CCS must be run by the analyst at a minimum interval of one CCS every 12 hours and at the end of the run. The response of the CCS should be within 25 percent of the same standard in the calibration curve.

3.2.5 Quality Control Check Standards (ICV) - a quality control check standard is prepared by diluting a commercially prepared composite mix of the methyl esters to a nominal concentration equivalent to STD A. in hexane. The ICV must be within 25% of the true value.

4.0 SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE

There are no special considerations required due to the nature of herbicides. The samples need to be chilled to 4 degrees C immediately following sampling.

4.2 STORAGE CONDITIONS

Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4 degrees C.

4.3 HOLDING TIMES

The holding time is 7 days from sampling to extraction and 40 days after extraction to analysis.

5.0 PROCEDURE

5.1 Sample Preparation

5.1.1 Extraction:

5.1.1.1 Using a 1 liter graduated cylinder, measure 1 liter (nominal) of sample, record the sample volume to the nearest 5 ml, and transfer it to a 2-liter separatory funnel. Check the pH with wide-range pH paper. Adjust the pH to less than 2 with sulfuric acid (1:1). Add 1.0 mL of surrogate solution to each sample, including QC samples.

5.1.1.1.1 QC samples are as follows:

MB - Use 1 liter USAEC Standard Water.

High Spike - (Prepare in duplicate) 1 liter USAEC Standard Water spiked with 1 mL of High Spike solution prepared as in Section 3.1.5.

Low Spike - 1 liter USAEC Standard Water spiked with 1 mL of Low Spike solution prepared as in Section 3.1.6.

Sample Matrix Spike - 1 liter of sample spiked with 1 mL of the High Spike Solution. **Sample Matrix spikes will only be prepared if requested by the project and at the frequency specified by the project.**

5.1.1.2 Add 150 mL of diethyl ether to the sample bottle, seal, and shake for 30 sec to rinse the walls. Transfer the solvent wash to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water layer for a minimum of 10 min. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Drain the aqueous phase into a 1-liter Erlenmeyer flask. Collect the solvent extract in a 250-mL ground-glass Erlenmeyer flask containing 2 mL of 37% KOH. Approximately 80 mL of the diethyl ether will remain dissolved in the aqueous phase.

5.1.1.3 Repeat the extraction two more times using 50 mL of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1-liter flask with each additional aliquot of extracting solvent.)

5.1.2 Hydrolysis:

5.1.2.1 Add 30 mL of reagent water, 5 mL of 37% KOH, and one or two clean boiling chips to the flask. Place a three-ball Snyder column on the flask, evaporate the diethyl ether on a water bath, and continue to heat for a total of 90 min.

5.1.2.2 Remove the flask from the water bath and allow to cool. Transfer the water solution to a 125-mL separatory funnel and check the pH. If the solution is not basic (pH > 10) add enough 37% KOH to basify it. Extract the basic solutions once with 40 mL and then twice with 20 mL of diethyl ether. Allow sufficient time for the layers to separate and discard the ether layer each time. The phenoxy acid herbicides remain soluble in the aqueous phase as potassium salts.

5.1.3 Solvent cleanup:

5.1.3.1 Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into a 250-mL Erlenmeyer flask, and pour the organic layer into a 125-mL Erlenmeyer flask containing about 5 g of acidified sodium sulfate. Repeat the extraction twice more with 10-mL aliquots of diethyl ether, combining all solvent in the 125-mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr. If the sodium sulfate clumps together, add more acidified sodium sulfate until it remains free flowing after remaining in contact with the extract for 2 hr.

5.1.3.2 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether

to complete the quantitative transfer.

5.1.3.3 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 10 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

5.1.3.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of diethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether.

5.1.4 Esterification: Bubbler method: Assemble the diazomethane bubbler (see Attachment I).

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

- Use a safety screen.
- Use mechanical pipetting aides.

- Do not heat above 90°C -- EXPLOSION may result.

- Avoid grinding surfaces, ground-glass joints, sleeve bearings, glass stirrers -- EXPLOSION may result.
- Store away from alkali metals -- EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

5.1.4.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% aqueous KOH, and 0.1-0.2 g Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 min or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 1-1.5 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 min of total esterification.

5.1.4.2 Remove the concentrator tube and loosely cap it with a Teflon lined cap. Store at room temperature in a hood for 20 minutes.

5.1.4.3 Unreacted diazomethane is remove by leaving the extracts, loosely capped, in the hood for at least 8 hours. If samples are to be analyzed the same day, the unreacted diazomethane is removed by bubbling nitrogen gas through the sample until the yellow color is removed. The extract is now ready for analysis by gas chromatography.

5.2 Instrumental Analysis

5.2.1 Perform the daily instrument calibration as described in Section 3.2.

5.2.2 Place the sample extracts in the autosampler and inject 2 uL of each sample extract on each column pair using the following procedure:

1. Inst. blank
2. Std. F
3. Std. E
4. Std. D
5. Std. C
6. Std. B
7. Std. A
8. QC Check Std. (ICV)
9. Inst. blank
10. Method Blank
11. Low Spike Control Sample
12. High Spike Control Sample
13. High Spike Control Sample (2)
14. Samples.......

    CCS (After a maximum of 10 samples including QC samples)
    Inst. Blank
    Samples..........
    CCS (After a maximum of 10 samples)
    Repeat for up to 24 hours and end with a CCS.

5.2.3 The analyst must check the response of the target analytes within each sample. If the response of an analyte exceeds the calibration range for that analyte the sample must be diluted and reanalyzed.

5.3 PEAK IDENTIFICATION

5.3.1 Retention Time Windows

5.3.1.1 Retention time windows for a method are established based on historical data of daily performance of the method or by using retention windows from a reference method. If a reference method with established windows is not available the windows are calculated by calculating the relative standard deviation of the retention variation throughout the run for all standards, control samples and continuing calibration standards and multiplying the result by three and rounded to 1 significant figure. The windows are expressed in absolute minutes where the retention variation is minimal throughout the chromatographic run and as a percentage of the retention time in methods whose variation is proportional to retention time. The retention window is applied to retention times from a specified standard during initial or daily calibration. These retention window values are entered into the method used for processing of the chromatographic data for computerized identification/rejection of detected peaks. The analyst can override the identification/rejection of a peak by providing documentation of his decision.

5.3.1.2 Retention time windows for Herbicide analysis will be set as $\pm$ 0.01 min for all peaks. A target response that falls in the window on either column shall be considered to be tentatively identified.

5.3.1.3 When a compound is tentatively identified the other coulmn is examined to determine if there is a target response in the retention window for that analyte. If there is a response that falls in the retention windows on both columns the compound shall be considered identified. However the analyst's judgement will heavily on the interpretation of the chromatograms and the analysts (with proper documentation)

will have the option of not identifying a peak due to peak shape, matrix background interference or other reasons that must be documented.

6.0 CALCULATIONS

6.1 Target responses are transferred to the Laboratory Data Management System, CLASS (Chemical Laboratory Analytical and Scheduling System), along with any relevant samples information. The concentration is calculated using the regression equation calculated by CLASS. Final samples results are corrected for sample volume or weight, extract volume, percent moisture for solid samples, dilution factors and any applicable conversion factors.

6.2 Peak Identification

Analyte response that lies within the established retention time will be considered to be tentatively identified. Analyst must use their judgement as to whether the peak may represent a target compound by examining such factors as peak shape, resolution from interferences and matrix "noise".

6.3 Analyte Quantitation

Peak areas or heights may be used to calculate analyte concentrations. The same technique must be used for both the standard curve and the samples analyte.

6.4 The concentration of each parameter is determined according to the following formula:

$$\text{Concentration (ug/L)} = \frac{A\ V_t}{V_s}$$

where:

A = Concentration of the parameter found in the sample extract by comparison with the appropriate quadratic calibration standard curve (micrograms per mL),
Vs = Weight sample extracted (1 Liter), and
Vt = Volume of final extract (10 mL).

Moisture content of the soil is sent to the USAEC data management system along with the ug/g wet weight concentration and any dilution factor.

7.0 DAILY QUALITY CONTROL

7.1 Control Samples

7.1.1 Method blanks will be prepared and analyzed, at a frequency of 1 standard method blank per lot, to verify that the laboratory is not a source of sample contamination.

7.1.2 Standard spikes consisting of all control analytes as defined in Section 3.1.6 will be prepared by spiking into USAEC Standard Water and analyzed, at a frequency of 1 low spike and two high spikes per sample lot, to verify laboratory performance.

7.1.3 Spikes of surrogates as defined in Section 3.1.5 will be spiked into all field and QC samples to observe the recovery effects in the environmental matrix.

7.1.4 Sample matrix spikes consisting of all control analytes as defined in Section 3.1.5 (Standard spikes) will be prepared, **only when requested and at the requested frequency**, by spiking the high standard spike solution into two separate aliquots of an actual sample. The sample to

be used may be designated by the client or laboratory coordinator. The sample matrix spike will be used to verify method applicability to the sample matrix.

7.2 Control Charts

Control charts are prepared using the percent recovery data from the high level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

7.2.1 Accuracy: Two-point average percent recovery for the high level spikes within each lot, and a three-point moving average percent recovery for the low level spikes within each lot.

7.2.2 Precision: Two-point average difference between the high concentration spike and a three-point moving average difference between the low concentration spikes.

7.2.3 For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken. Initial warning and control limits will be determined by USAEC using laboratory performance data.

7.2.4 Out-of-control situations to be addressed are specified in Section 8.7 of the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

7.2.5 See appendix L of U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993) for discussion of modified control limits.

8.0 REFERENCES

8.1 EPA Method 8150 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.2 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

9.0 ATTACHMENTS

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **GAS CHROMATOGRAPHIC ANALYSIS OF CHLORINATED HERBICIDES IN ENVIRONMENTAL SOIL SAMPLES (METHOD SW-846 8150 / LH11 MODIFIED) USAEC METHOD - HBG1 - SOIL**

TABLE OF CONTENTS

TITLE: **GAS CHROMATOGRAPHIC ANALYSIS OF CHLORINATED HERBICIDES IN ENVIRONMENTAL SOIL SAMPLES (METHOD SW-846 8150 / LH11 MODIFIED) USAEC METHOD - HBG1 - SOIL**

1.0 SUMMARY AND APPLICATION

1.1 SUMMARY

1.1.1 This Standard Operating Procedure (SOP) follows EPA SW-846 protocols with additional quality control requirements applicable for the CLASS 1 analysis as specified in the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993). The analysis procedure is based on SW-846 method 8150.

1.1.2 A known weight of soil sample (10 grams) is added to 10 mL of 10N KOH and 20 mL of methanol and shaken overnight. The sample is centrifuged, decanted. The procedure is repeated with 15 min. of shaking. Extracts are combined. Extraneous organic material is removed by solvent wash. The sample is acidified, and the chlorinated acids are extracted with methylene chloride by manually shaking in a separatory funnel. The acids are converted to their methyl esters using diazomethane as the derivatizing agent. Excess derivatizing reagent is removed.

1.1.3 The esters are determined by analyzing a 2 uL volume of extract. A temperature program is used to separate the analytes which are detected with an Electron Capture Detector (ECD). The results are reported as the acid equivalents.

1.2 APPLICATION

1.2.1 This SOP may be used to determine the following chlorinated acid herbicides by gas chromatography (GC).

Compound Name	Cas No.[a]	USAEC ACRONYM
2,4-D	94-75-7	24D
2,4-DB	94-82-6	24DB
2,4,5-T	93-76-5	245T
2,4,5-TP	93-72-1	245TP
Dalapon	75-99-0	DALA
Dicamba	1918-00-9	DCAMBA
Dichlorprop	120-36-5	DICP
Dinoseb	88-85-7	DINO
MCPA	94-74-6	MCPA
MCPP	93-65-2	MCPP
2,4 Dichlorophenyl-acetic acid (surrogate)	19719-28-9	DCAA

[a] Chemical Abstract Services Registry Number

1.2.2 The sensitivity of this method usually depends on the level of interferences rather than on instrumental limitations.

1.2.3 This SOP describes analytical conditions for a second gas chromatographic column that can be used to confirm the analysis made by the primary column.

1.2.4 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. Glassware must be scrupulously cleaned. The acid forms of the analytes are strong organic acid which react readily with alkaline subtances and can be lost during sample preparation. Glassware and glass wool must be acid rinsed with (1+9) hydrochloric acid and the sodium sulfate must be acidified with sulfuric acid prior to use to avoid analyte losses due to adsorption. Organic acids, especially chlorinated acids cause the most direct interference. Phenols also may interfere.

1.2.5 Reporting limits for Herbicides in soil are as follows:

Compound Name	Reporting Limit (ug/g)	Calibration Std Range (ng/mL) Low	High
2,4-D	0.01	10	100
2,4-DB	0.01	10	100
2,4,5-T	0.01	10	100
2,4,5-TP	0.01	10	100
Dalapon	0.01	10	100
Dicamba	0.01	10	100
Dichlorprop	0.01	10	100
Dinoseb	0.01	10	100
MCPA	0.2	200	2000
MCPP	0.2	200	2000

2.0 APPARATUS, CHEMICALS AND INSTRUMENTATION

2.1 APPARATUS

2.1.1 Extraction

2.1.1.1 Evaporative concentrator -- Kuderna-Danish, 250 mL flask and 10 mL volumetric receiver.

2.1.1.2 Snyder columns -- three-ball macro, one-ball micro.

2.1.1.3 Separatory funnels -- 250 mL, with telfon stopcocks and tapered ground-glass stoppers.

2.1.1.4 Pipettes -- 140 mm long and 5 mm i.d. glass disposable pipettes.

2.1.1.5 Microsyringes -- 10 mL.

2.1.1.6 Water bath

2.1.1.7 Erlenmeyer flask -- 250 mL with ground-glass mouth to fit Snyder columns.

2.1.2 Analysis

2.1.2.1 1 mL clear vials

2.1.2.2 Seals

2.1.2.3 9" Pasteur pipets

2.1.2.4 Crimper

2.1.2.5 Volumetric flasks - 25, 50, 100 mLs

2.1.2.6 Volumetric pipets - various sizes ranging from 0.5 to 20.0 mLs.

2.1.2.7 Amber bottles - 25 and 50 mL.

2.1.2.8 Micropipets - 50, 100 and 200 uL.

2.1.2.9 Analytical balance

2.1.2.10 Spatula

2.2 CHEMICALS

2.2.1 Extraction

2.2.1.1 Acetone, methanol, methylene chloride, methyl tert-butyl ether MTBE -- Pesticide quality or equivalent.

2.2.1.2 Diethyl ether -- Nanograde, redistilled if necessary.

2.2.1.3 Toluene -- reagent grade.

2.2.1.4 Sodium sulfate: (ACS) granular, acidified, anhydrous. Heat treat in a shallow tray at 400° C for a minimum of 4 hr to remove phthalates and other interfering organic substances. Acidify by slurring 100 g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH of the mixture. It must be below a pH of 4. Store at 130°C.

2.2.1.5 Carbitol, ACS grade (Diethylene glycol monoethyl ether or 2-(2-ethoxyethoxy) ethanol).

2.2.1.6 Diazald, ACS grade (N-methyl-N-nitroso-p-toluenesulfonamide).

2.2.1.7 Sulfuric acid, concentrated, ACDD grade.

2.2.1.8 Potassium Hydroxide (KOH) , pellets -- ACS grade.

2.2.1.9 Potassium hydroxide.

2.2.1.10 Magnesia-silica gel -- PR grade.

2.2.1.11 Glass wool -- acidified, filtering grade.

2.2.1.12 Hexane -- pesticide.

2.2.1.13 USAEC Standard Soil

2.2.2 Analysis

2.2.2.1 Solvents

2.2.2.1.1 Methanol - Pesticide grade.

2.2.2.1.2 Methyl tert-butyl ether (MTBE) - Pesticide grade.

2.2.2.1.3 Hexane - Pesticide grade

2.2.2.2 Stock Standard solutions - available from commercial vendors.

2.2.2.3 Neat - available from ChemServe or equivalent, as 99.9% pure. Chemicals of a purity 96% or less must be corrected for purity.

2.2.2.4 Solutions - available from Crescent or equivalent, as 1 mg/ml.

2.2.2.5 Stock Surrogate - 2,4-Dichlorophenyl acetic acid, 99.9%, available from Aldrich or equivalent

2.3 INSTRUMENTATION (GAS CHROMATOGRAPH)

2.3.1 Hewlett Packard 5890 Gas Chromatograph or equivalent equipped with dual Ni-63 ECD's, dual auto injectors, and capable of temperature programming is used. The GC must be accommodate two dissimilar columns. A computerized data system (HP3359) is used to collect chromatographic data.

2.3.2 Columns

2.3.2.1 Primary: DB-17 30 meter x 0.25 mm fused silica capillary column with 0.25 um film

2.3.2.2 Secondary: DB-5 30 meter x 0.25 mm fused silica capillary column with 0.25 um film

2.3.2.3 Gas Chromatographic conditions:

Injector temperature: 250° C

Detector temperature: 300° C

Column temperature ramp: 50° C/1 min to 150° C at 20°C/min, hold for 2 mins; 150°C to 200°C @ 2°C/min, hold for 0 mins; 200°C to 280°C @ 50° C/min, hold for 11 min.

Program specified is typically used. However, the temperature program may need modification to avoid interferences. This would depend upon matrix interferences. **ANY MODIFICATION MUST BE CLEARLY DOCUMENTED.**

Gases: Carrier Gas - Helium, ultra pure carrier, flow of 1 to 2 mL per minute.

Make up Gas - 5% Methane/Argon, flow of 40 to 50 mL per minute.

3.0 PREPARATION OF STANDARDS AND CALIBRATION

3.1 CALIBRATION STANDARDS

3.1.1 Stock Standard solutions - Stock standard solutions are prepared from pure standard materials.

3.1.1.1 Prepare stock standard solutions by accurately weighing 25 mg of the pure acids into a 25 mL volumetric flask. Dissolve and bring to volume in MTBE. Final concentration will be, nominally, 1 mg/mL (1000 ug/ml).

3.1.1.2 Five milliliters of each of the stock standard solutions (25mL of MCPP and MCPA) is derivatized by bubbling diazomethane in the solution as described below:

3.1.1.2.1 Assemble the diazomethane generator (ATTACHMENT I) in a hood.

3.1.1.2.1 Add 20 mL (2 inches or same height as Tube 2) of ethyl ether to Tube 1. Add 5 mL of ethyl ether, 5 mL of carbitol®, 7.5 mL of 37% aqueous KOH, and 1g diazald to Tube 2. Immediately place the exit tube into the concentrator tube containing the stock standard solution. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the first stock solution for 1 minute. Immediately remove first stock solution, replace

disposable pipette tip and continue to the next solution. Diazomethane reaction mixture can be used to esterify about 6 samples. When samples stop turning yellow add about 2 or 3 scoops of Diazald to tube 2 and about 4 or 5 more samples can be esterified before emptying and rinsing tubes.

3.1.1.3 Transfer the stock standard solution into an amber bottle with a teflon lined screw cap. Store at 4° C and protect from light.

3.1.1.4 Stock Standard solutions must be replace after 1 year, or sooner, if comparison with check standards indicates a problem.

3.1.2 Intermediate Stock solutions

3.1.2.1 Intermediate Stock A - Pipet 1 mL of each stock standard solution into a 100 mL volumetric flask. Pipet 2 mLs of the surrogate stock standard solution (DCAA) (Section 3.1.5) and dilute with hexane to volume in a 50 ml volumetric flask (use 20 mLs of MCPP and MCPA). Final concentration will be 20 ug/mL (10,000 ng/ml) nominal (200 ug/mL for MCPP and MCPA and 20 ug/mL for DCAA).

3.1.2.2 Intermediate Stock B - Pipet 10 mL of Intermediate Stock A (3.1.2.1) into a 100 mL volumetric flask and dilute to volume with hexane. Final concentration will be 1000 ng/ml nominal (20,000 ng/mL for MCPP and MCPA and 2000 ng/mL for DCAA).

3.1.3 Working Standards - Seven calibration standards for each parameter of interest prepared through dilution of the secondary stock with hexane. They are prepared in 100 mL volumetric flasks by adding the volumes of standards as specifed below to achieve the following nominal

concentrations:

To Prepare	Std Used	Volume Used (mL)	Dilute to (mL)	NOMINAL CONCENTRATIONS MCPA/MCPP (ng/mL)	All Others (ng/mL)	DCAA (Surr.) (ng/mL)
STD G	Int.Stock B	0.1	50	40	2	4
STD F	Int.Stock B	0.2	50	80	4	8
STD E	Int.Stock B	0.5	50	200	10	20
STD D	Int.Stock B	1	50	400	20	40
STD C	Int.Stock B	2.5	50	1000	50	100
STD B	Int.Stock B	4	50	1600	80	160
STD A	Int.Stock B	5	50	2000	100	200

Working standards must be prepared every six months, or sooner, if comparison with a check standard indicates a problem.

3.1.4 Quality Control Check Standards (ICV) - a quality control check standard is prepared by diluting a commercially prepared composite mix of the methyl esters to a nominal concentration equivalent to STD A. in hexane. The ICV must be within 25% of the true value.

3.1.5 Surrogate Standards - The analyst should monitor the performance of the extraction, cleanup (when used), analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard spike sample, sample matrix spike and reagent water blank with 2,4-Dichlorophenyl acetic acid (DCAA). Prepare a stock standard solution by accurately weighing 25 mg of the DCAA into a 25 mL volumetric flask. Dissolve and bring to volume in methanol. Final concentration will be, nominally, 1 mg/mL (1000 ug/ml).

3.1.5.1 Secondary Stock Surrogate solution - Pipet 1 mL of primary stock surrogate solution into a 100 mL volumetric flask and fill to volume with methanol. Final concentration is 10 ug/mL (10,000 ng/mL) 2,4-Dichlorophenyl acetic acid.

3.1.5.2 Working solution - Pipet 5.0 mLs of the secondary stock surrogate solution into a 50 mL volumetric flask and fill to

volume with methanol. Final concentration 1,000 ng/mL. A 1 mL aliquot must be spiked into all samples and QC samples.

3.1.6 Spike Solutions

3.1.6.1 Working Spike solution - A working spike solution should be made from a different source than the Stock Standard solution. If it is not possible to find another source, then use the same source, but from a different lot. Pipet 2 mL of each stock standard solution into a 100 mL volumetric flask. Dilute to volume with methanol. Final concentration will be 20 ug/ml (20,000 ng/mL) nominal. Spike Analytes are as follows:

2,4-D
2,4-DB
2,4,5-T
2,4,5-TP
Dichlorprop
Dicamba

3.1.6.2 High Spike Solution - A high spike solution is prepared by adding 4.0 mL of the Working Spike solution to a 100 mL volumetric flask. Bring to volume with methanol. The nominal concentration for each analyte is 800 ng/mL (or 800 ug/L).

3.1.6.3 Low Spike solution - A low spike solution is prepared by adding 1.0 mL of the Working Spike solution to a 100 mL

volumetric flask. Bring to volume with methanol. The nominal concentration for each analyte is 200 ng/mL (or 200 ug/L).

Spiking levels in 10 g of USAEC soil are as follows:

Compound Name	Spike Level (ug/g) Low	High
2,4-D	0.02	0.08
2,4-DB	0.02	0.08
2,4,5-T	0.02	0.08
2,4,5-TP	0.02	0.08
Dichlorprop	0.02	0.08
Dicamba	0.02	0.08

3.2 INSTRUMENT CALIBRATION (INITIAL AND DAILY)

3.2.1 Set-up the GC according to the analytical conditions specified in Section 2.3.3.3 and load the samples onto the autosampler.

3.2.2 Use the external calibration technique to calibrate the GC system.

3.2.3 Establish retention times for all analytes and for both columns used for analysis.

3.2.4 Continuing Calibration Check Standard (CCS) - A CCS (STD A) must be run by the analyst at a minimum interval of one every 12 hours and at the end of the run. The response of (STD A) should be within 25 percent of the response of the same standard in the calibration curve.

4.0 SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE

There are no special considerations required due to the nature of herbicides. The samples need to be chilled to 4 degrees C immediately following sampling.

4.2 STORAGE CONDITIONS

Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4 degrees C.

4.3 HOLDING TIMES

The holding time is 7 days from sampling to extraction and 40 days after extraction to analysis.

5.0 PROCEDURE

5.1 Sample Preparation

5.1.1 Extraction:

5.1.1.1 Weigh 10 grams of soil into 40 mL vial, add 1.0 mL of surrogate solution to each sample (including QC samples) and allow to stand for an hour, add 10 mL of 10N KOH and 20 mL of methanol, then shake overnite (at least 16 hours). Centrifuge 15 min. at 1000 rpm then decant solvent into a 250 mL separatory funnel. Repeat addition of 10 mL of 10N KOH, 20 mL of methanol, shake 15 min., cetrifuge and decant, combining with the previous extract.

5.1.1.1.1 QC samples are as follows:

MB - Use 10 g USAEC Standard Soil.

High Spike - (Prepare in duplicate) 10 g USAEC Standard Soil spiked with 1 mL of High Spike solution prepared as in Section 3.1.6.2.

Low Spike - 10 g USAEC Standard Soil spiked with 1 mL of Low Spike solution prepared as in Section 3.1.6.3.

Sample Matrix Spike - 10 g of sample spiked with 1 mL of the High Spike Solution. **Sample Matrix spikes will only be prepared if requested by the project and at the frequency specified by the project.**

5.1.1.2 Add 50 mL of methylene chloride to the separatory funnel and extract the sample by vigorous shaking for 2 minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minute. If the emulsion interface between layers is more than one third the

volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Discard the methylene chloride phase.

5.1.1.3 Add 10 mL of 12 N Sulfuric Acid to the sample, and shake to mix. Check the pH of the sample which should be approximately 1. Add additional acid if needed to adjust pH.

5.1.1.4 Extract the sample three times with methylene chloride (as in Step 5.1.1.2) and drain the methylene chloride through acidified sodium sulfate and acidified glass wool into a Kuderna-Danish concentrator.

5.1.1.5 Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL ethyl ether to the top. Place the K-D apparatus on a hot water bath, 60 to 65 degrees C, so that the concentrator tube is partially immersed in the hot water, and the entire lower surface of the flask is bathed in hot vapor. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Then add 200 uL of methanol and solvent exchange to 1 mL of ether. The sample is then ready for derivitization.

5.1.2 Esterification

5.1.2.1 Assemble the diazomethane generator (ATTACHMENT I) in a hood.

5.1.2.2 Add 20 mL (2 inches or same height as Tube 2) of ethyl ether to Tube 1. Add 5 mL of ethyl ether, 5 mL of carbitol®, 7.5 mL of 37% aqueous KOH, and 1g diazald to

Tube 2. Immediately place the exit tube (a disposable pipette) into the concentrator tube containing the sample extract. Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract. When the extract turns yellow, and the color persists, remove the exit tube, replace the disposable tip, and continue to the next extract. If the yellow color does not persist for at least 20 min. the extract must be rederivatized. If the extract is deeply colored and the color change cannot be discerned, derivatize another extract (in which the derivatization color change is easily discernable) first. Note the time required for derivatization of that sample and double the derivatization time for the problem sample. Diazomethane reaction mixture can be used to esterify about 3-4 samples. When samples stop turning yellow add about 2 or 3 scoops (approxiamtely 1 to 1.5 grams) of Diazald to tube 2 and about 4 or 5 more samples can be esterified before emptying and rinsing tubes.

5.1.2.3 Unreacted diazomethane is remove by leaving the extracts, loosely capped, in the hood for at least 8 hours. If samples are to be analyzed the same day, the unreacted diazomethane is removed by bubbling nitrogen gas through the sample until the yellow color is removed.

5.1.2.4 Adjust the sample volume to 10 mL with hexane.

5.2 Instrumental Analysis

5.2.1 Perform the daily instrument calibration as described in Section 3.2.

5.2.2 Place the sample extracts in the autosampler and inject 2 uL of each sample extract on each column pair using the following procedure:

1. Inst. blank
2. Std. F
3. Std. E
4. Std. D
5. Std. C
6. Std. B
7. Std. A

8. QC Check Std. (ICV)
9. Inst. blank
10. Method Blank
11. Low Spike Control Sample
12. High Spike Control Sample
13. High Spike Control Sample (2)
14. Samples.......
    CCS (After a maximum of 10 hours of samples including QC samples)
    Inst. Blank
    Samples..........
    CCS (After a maximum of 10 hours of samples)
    Repeat for up to 24 hours and end with a CCS.

5.2.3 The analyst must check the response of the target analytes within each sample. If the response of an analyte exceeds the calibration range for that analyte the sample must be diluted and reanalyzed.

5.3 PEAK IDENTIFICATION

5.3.1 Retention Time Windows

5.3.1.1 Retention time windows for a method are established based on historical data of daily performance of the method or by using retention windows from a reference method. If a reference method with established windows is not available the windows are calculated by calculating the relative standard deviation of the retention variation throughout the run for all standards, control samples and continuing calibration standards and multiplying the result by three and rounded to 1 significant figure. The windows are expressed in absolute minutes where the retention variation is minimal throughout the chromatographic run and as a percentage of the retention time in methods whose variation is proportional to retention time. The retention window is applied to retention times from a specified standard during initial or daily calibration. These retention window values are

entered into the method used for processing of the chromatographic data for computerized identification/rejection of detected peaks. The analyst can override the identification/rejection of a peak by providing documentation of his decision.

5.3.1.2 Retention time windows for Herbicide analysis will be set as $\pm$ 0.01 min for all peaks. A target response that falls in the window on either column shall be considered to be tentatively identified.

5.3.1.3 When a compound is tentatively identified data from the other column are examined to determine if there is a target response in the retention window for that analyte. If there is a response that falls in the retention windows on both columns the compound shall be considered identified. However the analyst's judgement will heavily on the interpretation of the chromatograms and the analysts (with proper documentation) will have the option of not identifying a peak due to peak shape, matrix background interference or other reasons that must be documented.

6.0 CALCULATIONS

6.1 Target responses are transferred to the Laboratory Data Management System, CLASS (Chemical Laboratory Analytical and Scheduling System), along with any relevant samples information. The concentration is calculated using the regression equation calculated by CLASS. Final samples results are corrected for sample volume or weight, extract volume, percent moisture for solid samples, dilution factors and any applicable conversion factors.

6.2 Peak Identification

Analyte response that lies within the established retention time will be considered to be tentatively identified. Analyst must use their judgement as to whether the peak may represent a target compound by examining such factors as peak shape, resolution from interferences and matrix "noise".

6.3 Analyte Quantitation

Peak areas or heights may be used to calculate analyte concentrations. The same technique must be used for both the standard curve and the samples analyte.

6.4 The concentration of each parameter is determined according to the following formula:

$$\text{Concentration(ug/g)} = \frac{A\ V_t}{W_s}$$

where:

A = Concentration of the parameter found in the sample extract by comparison with the appropriate quadratic calibration standard curve (micrograms per mL),
Ws = Weight sample extracted (10 grams), and
Vt = Volume of final extract (10 mL).

Moisture content of the soil is sent to the USAEC data management system along with the ug/g wet weight concentration and any dilution factor.

7.0 DAILY QUALITY CONTROL

7.1 Control Samples

7.1.1 Method blanks will be prepared and analyzed, at a frequency of 1 standard method blank per lot, to verify that the laboratory is not a source of sample contamination.

7.1.2 Standard spikes consisting of all control analytes as defined in Section 3.1.6 will be prepared by spiking into USAEC Standard Soil and analyzed, at a frequency of 1 low spike and two high spikes per sample lot, to verify laboratory performance.

7.1.3 Spikes of surrogates as defined in Section 3.1.5 will be spiked into all field and QC samples to observe the recovery effects in the environmental matrix.

7.1.4 Sample matrix spikes consisting of all control analytes as defined in Section 3.1.6 (Standard spikes) will be prepared, **only when requested and at the requested frequency**, by spiking the high standard spike solution into two separate aliquots of an actual sample. The sample to be used may be designated by the client or laboratory coordinator. The sample matrix spike will be used to verify method applicability to the sample matrix.

7.2 Control Charts

Control charts are prepared using the percent recovery data from the high level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

7.2.1 Accuracy: Two-point average percent recovery for the high level spikes within each lot, and a three-point moving average percent recovery for the low level spikes within each lot.

7.2.2 Precision: Two-point average difference between the high concentration spike and a three-point moving average difference between the low concentration spikes.

7.2.3 For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken. Initial warning and control limits will be determined by

USAEC using laboratory performance data.

7.2.4 Out-of-control situations to be addressed are specified in Section 8.7 of the U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

7.2.5 See appendix L of U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993) for discussion of modified control limits.

8.0 REFERENCES

8.1 EPA Method 8150 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.2 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects (May 1993).

8.3 Determination of Herbicides in Soil by Electron Capture Gas Chromatography USTAHAMA METHOD NUMBER: LH11

9.0 ATTACHMENTS

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **DETERMINATION OF EXPLOSIVES IN WATER BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (METHOD EXL1-W)**

TABLE OF CONTENTS

TITLE: DETERMINATION OF EXPLOSIVES IN WATER BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (METHOD EXL1-W)

1. SUMMARY AND APPLICATION

1.1 SUMMARY

The method employs solid phase extraction of 500 mL of an environmental water sample using a tube packed with Porapak R. The water sample is spiked with a surrogate (3,4-Dinitrotoluene) prior to the solid phase extraction. The target compounds are desorbed with 3 mL of acetonitrile and diluted to a final volume of 10 mL with water. The compounds are separated by high performance liquid chromatography (HPLC) using isocratic elution and detected using ultraviolet (UV) absorbance at 250 nanometers (nm).

1.2 APPLICATION

1.2.1 This method is applicable to all environmental water matrices.

1.2.2 This method is applicable to the Class 1 analysis of the following nitroaromatic organic compounds in environmental water samples:

<u>Analytes</u>
1,3-Dinitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
HMX (octahydro-1,3,5,7-tetranitro-s-tetrazocine)
Nitrobenzene
RDX (hexahydro-1,3,5-trinitro-s-triazine)
Tetryl (N-methyl-N,2,4,6-tetranitrobenzenamine)
1,3,5-Trinitrobenzene
2,4,6-Trinitrotoluene
4-Amino-2,6-Dinitrotoluene
2-Amino-4,6-Dinitrotoluene
2-Nitrotoluene
3-Nitrotoluene
4-Nitrotoluene

1.2.3 The Chemical Abstract Service (CAS) numbers and USAEC acronyms for the explosives are presented in Table 1-1.

1.2.4 The reporting limits and lower and upper standard ranges for the explosives are listed in Table 1-2.

1.2.5 Interferences

1.2.5.1 Any materials which are adsorbed from water on the cartridge, coelute with the explosives through the HPLC column, and which absorb ultraviolet radiation at 250 nm may cause interferences. Carryover from analysis of a highly contaminated sample can result in apparent contamination of the succeeding samples analyzed. Such contamination is often manifest by the presence of unusually broad chromatographic peaks nested among narrower peaks. This interference is minimized by analyzing apparent heavily contaminated samples at the end of a run, or running blanks after heavily contaminated samples until carryover is removed, and/or rinsing the system with a mobile phase containing a high proportion of organic modifier until the contamination is removed.

1.2.6 Analysis Rate

1.2.6.1 After instrument calibration, one analyst can analyze approximately 12 samples in an 8-hour day.

1.2.7 Safety Information

1.2.7.1 The target compounds in this method are toxic explosives and some are known carcinogens, e.g. 2,6-Dinitrotoluene. The preparation of all standards should be performed in a laboratory hood. Adequate dermal protection must be used when handling samples and standards. Most of these compounds are either primary or secondary explosives and should be handled with care to avoid contact with electrostatic shocks or impacts. Tetryl and RDX have intermediate sensitivity between

initiating explosives and explosives used as bursting charges. Tetryl is toxic when taken internally or by skin contact. RDX, HMX, and 246TNT are used as bursting charge explosives. Although 246TNT is less sensitive to friction and impact than many other high explosives, it can be detonated with moderate force when confined between metal surfaces such as on the threads of bolts. 246TNT will form sensitive materials in the presence of alkalies.

Table 1-1. USAEC Acronyms and CAS Numbers for Explosives

ANALYTE	ACRONYM	CAS NUMBER
HMX	HMX	2691-41-0
RDX	RDX	121-84-4
1,3,5-Trinitrobenzene	135TNB	25377-32-6
1,3-Dinitrobenzene	13DNB	99-65-01
Tetryl	TETRYL	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	246TNT	118-96-7
4-Amino-2,6-Dinitrotoluene	4A26DT	1946-51-0
2-Amino-4,6-Dinitrotoluene	2A46DT	118-96-7
2,6-Dinitrotoluene	26DNT	606-20-2
2,4-Dinitrotoluene	24DNT	121-14-2
2-Nitrotoluene	2NT	88-72-2
4-Nitrotoluene	4NT	99-99-0
3-Nitrotoluene	3NT	99-08-1

Table 1-2. Reporting Limits and Lower and Upper Standard Range for Explosives in Water by Method XXXX.

Parameter	Reporting Limit (μg/L)	Upper Reporting Limit (μg/L)	Lower Standard (ng/mL)	Upper Standard (ng/mL)
HMX	0.20	81.6	8.16	4080
RDX	0.20	84.0	8.39	4200
1,3,5-Trinitrobenzene	0.10	44.4	4.45	2220
1,3-Dinitrobenzene	0.10	29.6	2.97	1480
Tetryl	1.00	45.2	4.52	2260
Nitrobenzene	0.10	37.0	3.70	1850
2,4,6-Trinitrotoluene	0.10	41.8	4.18	2090
4-Amino-2,6-Dinitrotoluene	0.10	45.0	4.49	2250
2-Amino-4,6-Dinitrotoluene	0.10	36.4	3.65	1820
2,6-Dinitrotoluene	0.07	45.8	4.0	2290
2,4-Dinitrotoluene	0.06	30.6	3.06	1530
2-Nitrotoluene	0.20	68.4	6.84	3420
4-Nitrotoluene	0.20	92.0	9.20	4600
3-Nitrotoluene	0.20	79.2	7.92	3960

2.0 APPARATUS AND CHEMICALS

2.1 GLASSWARE/HARDWARE

2.1.1 Sorbent Cartridge - 6 mL Disposable Solid Phase Extraction Columns, PORAPAK Rdx, 0.5 gram, (Waters, Milford, MA.).

2.1.2 Baker 10 Solid Phase Extraction System, (J.T. Baker, Phillipsburg, NJ) including manifold, 75 mL reservoirs and adapters.

2.1.3 Class A Volumetric flasks - 10, 100 and 500 mL.

2.1.4 Class A Volumetric pipets - 0.5, 1.0, 2.0 mL.

2.1.5 Aspirator.

2.1.6 Disposable micro pipets - 25, 50, 100 and 200 μL.

2.2 INSTRUMENTATION AND INSTRUMENTAL CONDITIONS

PRIMARY ANALYSIS

2.2.1 HPLC - Shimadzu model SCL-10A HPLC with Shimadzu model SIL-10A autosampler (or equivalent).

2.2.2 Detector: Shimadzu SPD-10A variable wavelength UV detector set at 250 nm.

2.2.3 Column: Phenomenex ODS (octadecylsilane), reverse-phase column, 25 cm length x 4.6 mm I.D., 5 micrometers (μm) particle size (Phenomenex, Inc. Torrance, Ca.).

2.2.4 Mobile phase: Isocratic, 55% methanol/45% water (v/v).

2.2.5 Flow rate: 0.8 mL/min.

2.2.6 Injection volume: 500 μL.

2.2.7 Temperature: Ambient.

CONFIRMATION ANALYSIS

2.2.8 Shimadzu model LC-6A with Shimadzu SIL-6A autosampler or equivalent.

2.2.9 Detector: Shimadzu SPD-6A at 250 nm.

2.2.10 Column: Zorbax Cyano, 250 x 4.6 mm, 5 μm packing.

2.2.11 Mobile phase: Isocratic, 50/50 (v/v) methanol/water.

2.2.12 Flow rate: 1 mL/min..

2.2.13 Injection volume: 500 μL.

2.2.14 Temperature: Ambient.

2.3 CHEMICALS

2.3.1 Methanol (HPLC grade - American Burdick & Jackson, McGaw Park, IL).

2.3.2 Water (ASTM Type II/HPLC grade - American Burdick & Jackson, McGaw Park, IL).

2.3.3 Acetonitrile (HPLC grade - American Burdick & Jackson, McGaw Park, IL).

2.3.4 Acetone (HPLC grade - American Burdick & Jackson, McGaw Park, IL).

2.4 STANDARDS

2.4.1 The standards used for target compound certification and calibration are USAEC supplied standard analytical reference materials (SARMS) except for the additional compounds added to the method (2A46DT, 4A26DT, 2NT, 3NT, 4NT and the surrogate 34DNT). Standard materials for the additional compounds were obtained from 2 sources: Aldrich Chemical Co. (2NT, 3NT, 4NT, and 34DNT); and, the Naval Surface Weapons Center -NSWC (2A46DT and 4A26DT). HPLC

characterizations of the non USAEC SARMS showed that only the compounds of interest were present. The USAEC SARMS used for this certification, and their lot numbers are listed below:

Analyte	SARM LOT NUMBER
1,3-Dinitrobenzene	2250
2,4-Dinitrotoluene	1147
2,6-Dinitrotoluene	1148
HMX	1217
Nitrobenzene	2177
RDX	1130
Tetryl	1149
1,3,5-Trinitrobenzene	1154
2,4,6-Trinitrotoluene	1129

3.0 CALIBRATION

Table 3-1 summarizes the concentration of calibration stock solutions and preparation of intermediate calibration standards. Table 3-2 summarizes the preparation and concentration of calibration standards used for initial and daily calibration. To summarize the information presented, individual and separate primary stock solutions (SPSS's) are prepared for each compound by dissolving a known amount of the SARM in 10 or 25 mL of acetonitrile. The nominal concentrations of these SPSS range from 500 to 3500 μg/mL. Two subsets of combined intermediate stock solutions are prepared to prevent degradation due to specific combinations of compounds. These two stock solutions are made up in acetonitrile. The range of concentrations in these two solutions is from 15 - 50 μg/mL. A 10 mL final volume of each calibration standard is prepared by dilution of the stocks to have a 30% acetonitrile concentration to match the acetonitrile concentrations in the final sample extracts.

3.1 INITIAL CALIBRATION

3.1.1 Preparation of Standards

Table 3-1 presents the procedure for preparing separate primary stock solutions, combined intermediate stock solutions and Tetryl calibration standards used for preparation of initial and daily calibrations during actual sample analysis. For initial calibration, Standards E2, E5, D, D2, D5, C, C2,

B and a blank described in Table 3-2 are prepared. These solutions are prepared fresh as needed but not stored for use longer than one month at 4° ± 2°C (10 mL of standard usually lasts 8 runs). The SPSS are prepared fresh every 12 months and stored in the dark at 4° ± 2 °C. Tetryl needs to be made fresh if degradation is evident but at least every 12 months. Each separate stock solution is made to volume with acetonitrile. The combined intermediate solutions are prepared fresh every 6 months (if 2 separate Stock A solutions are not made, degradation of some compounds may occur). HPLC-grade water is used for dilution to final volumes for the composite calibration standards (acetonitrile concentrations need to be no greater than 30%). Daily calibration standards are E2, D5, B and a blank as outlined in Table 3-2.

3.1.2 Instrument Calibration

3.1.2.1 Inject 500 μL of each calibration standard presented in Table 3-2, and analyze a reference standard following calibration and at the end of the run. Instrument conditions and the column are described in Sec. 2-2.

3.1.3 Independent Reference Standard

Reference materials are available for verification from Accustandard and Crescent Chemicals and are used for verification of the standard curve.

3.1.3.1 The independent reference must be analyzed with the initial calibration run and the results must be within ± 25% of the expected value. If the analysis of the independent reference standard fails, the source of the problem must be identified and corrected. The results of the second analysis of the independent reference standard must be within the acceptable limits before the analysis of samples may proceed. Since a new initial calibration is not performed daily, a reference is required at least weekly.

Table 3-1. Concentration of Primary and Intermediate Stock Solutions

ANALYTE	MASS (mg)	VOLUME (mL)	CONCENTRATION (μg/mL)	Volume (mL)	Final Volume (mL)	Intermediate Stock I Conc. (μg/mL)
HMX	85.0	25	3400	0.3	25	40.80
RDX	43.8	25	1748	0.6	25	41.95
1,3,5-Trinitrobenzene	55.5	25	2224	0.25	25	22.24
1,3-Dinitrobenzene	46.5	25	1856	0.2	25	14.85
2,4-Dinitrotoluene	38.3	25	1528	0.25	25	15.28
Nitrobenzene	115.8	25	4628	0.1	25	18.51
2,4,6-Trinitrotoluene	26.0	25	1044	0.5	25	20.88

ANALYTE	MASS (mg)	VOLUME (mL)	CONCENTRATION (μg/mL)	Volume (mL)	Final Volume (mL)	Intermediate Stock II Conc. (μg/mL)
3,4-Dinitrotoluene*	40.0	25	1598	0.5	25	31.96
4-Amino-2,6-Dinitrotoluene	23.4	25	936	0.6	25	22.46
2-Amino-4,6-Dinitrotoluene	28.5	25	1140	0.4	25	18.24
2,6-Dinitrotoluene	57.3	25	2288	0.25	25	22.88
2-Nitrotoluene	33.0	25	1316	0.65	25	34.22
4-Nitrotoluene	57.5	25	2300	0.5	25	49.00
3-Nitrotoluene	49.5	25	1980	0.5	25	39.60

ANALYTE	MASS (mg)	VOLUME (mL)	CONCENTRATION (μg/mL)	Volume (mL)	Final Volume (mL)	Intermediate Stock Conc. (μg/mL)
Tetryl	56.5	25	2260	0.5	10	113.0

*Surrogate

3.2 DAILY CALIBRATION.

3.2.1 Preparation of Standards: Standards E2, E5, D, D2, D5, C, C2, B, and a blank are prepared in 30% Acetonitrile/70% Water from solutions in Table 3-2.

Table 3-2. Preparation of Daily Calibration Standards

Standard	E2	E5	D	D2	D5	C	C2	B
Volume, mL	1.0	0.5	1.0	0.2	0.5	1.0	2.0	1.0 of I and II, 0.2 of Tetryl
Final Volume, mL	10	10	10	10	10	10	10	10
Solution	D2	C	C	B	B	B	B	I, II and Tetryl
HMX	8.16	20.4	40.8	81.6	204	408	816	4080
RDX	8.39	21.0	42.0	83.9	210	420	839	4200
TNB	4.45	11.1	22.2	44.5	111	222	445	2220
DNB	2.97	7.42	14.9	29.7	74.2	149	297	1490
TETRYL	4.52	11.3	22.6	45.2	113	226	452	2260
NB	3.70	9.26	18.5	37.0	92.6	185	370	1851
3,4-DNT	6.39	16.0	32.0	63.9	160	320	639	3200
TNT	4.18	10.4	20.9	41.8	104	209	418	2090
4A26DNT	4.49	11.2	22.5	44.9	112	225	449	225
2A46DNT	3.65	9.12	18.2	36.5	91.2	182	365	1824
26DNT	4.58	11.4	22.9	45.8	114	229	458	2290
24DNT	3.06	7.64	15.3	30.6	76.4	153	306	1530
2NT	6.84	17.1	34.2	68.4	171	342	684	3422
4NT	9.20	23.0	46.0	92.0	230	460	920	4600
3NT	7.92	19.8	39.6	79.2	198	396	792	3960

3.2.2 Daily Instrument Calibration and Calibration Checks

At the beginning of each daily analytical run after initial calibration, inject 500 μL of the three daily calibration standards. Found concentrations are determined from the linear regression equations of initial calibration, therefore the percent recovery (100*Found/Target) must be within 25% of the true value (100%). After every seven lots, a new initial calibration curve is run.

3.2.3 Analysis of Continuing Calibration Data

Continuing calibration will be performed every 12 hours and at the end of the analytical run. The response of the target compounds in the continuing calibration and end run standards (B) must be less than 25 percent different from response factors obtained from Standard B analyzed at the beginning of the day. If the response is greater than 25 percent different, the standard will be reanalyzed. If reanalysis still fails the 25-percent criterion, a new initial calibration must be performed and all analyses since the last acceptable calibration must be repeated.

3.3 DAILY QUALITY CONTROL - Spike Solution Preparation

3.3.1 Control Samples

Daily quality control samples consist of a standard matrix method blank (ASTM Type I water), a single low level spike at approximately twice the certified reporting limit and duplicate high spikes at 10 times the low spike. These quality control samples should be carried throughout the entire method at the same time samples are run. Table 3-3 documents the preparation of stock spiking solutions and preparation of spiking solutions. Separate Primary Stock Standards (SPSS) at various concentrations near 1000 μg/mL are weighed using approximately 10 mg of each compound and diluted to 10 mL with acetonitrile. Each SPSS solution is diluted to prepare a combined intermediate stock solution for the low and high spikes as presented in Table 3-3.

Table 3-3. Preparation of Daily Control Spike Solutions

Analyte	Mass (mg)	Vol. (mL)	Conc., mg/mL	Intermediate			High Spike			Low Spike		
				Vol., mL	mL	Conc., µg/L	Vol., mL	mL	Conc., µg/mL	Vol., mL	mL	Conc., ug/ml
RDX	10	10	1.0	.4	10	40	1.0	10	4.0	1	10	0.4
135TNB	10	10	1.0	.2	10	20	1.0	10	2.0	1	10	0.2
NB	10	10	1.0	.2	10	20	1.0	10	2.0	1	10	0.2
246TNT	10	10	1.0	.2	10	20	1.0	10	2.0	1	10	0.2
2A46DT	10	10	1.0	.2	10	20	1.0	10	2.0	1	10	0.2
24DNT	10	10	1.0	.12	10	12	1.0	10	1.2	1	10	0.12
13DNB	10	10	1.0	.2	10	20	1.0	10	2.0	1	10	0.2
2NT	10	10	1.0	.4	10	40	1.0	10	4.0	1	10	0.4
3NT	10	10	1.0	.4	10	40	1.0	10	4.0	1	10	0.4
4NT	10	10	1.0	.4	10	40	1.0	10	4.0	1	10	0.4

0.5 mL of the spike solutions are added to 500 mL of ASTM Type II standard water to prepare the 2 high and 1 low daily control spike.

Table 3.4 Concentration of Daily Control Spikes

Analyte	Low Spike Target (μg/L)	High Spike Target (μg/L)
RDX	0.40	4.2
135TNB	0.20	2.2
NB	0.20	1.9
246TNT	0.20	2.1
2A46DT	0.20	1.8
24DNT	0.12	1.2
13DNB	0.20	1.4
2NT	0.40	3.4
3NT	0.40	4.0
4NT	0.40	4.6

3.3.2 Surrogate Spike: The surrogate stock spiking solution is prepared by weighing 62.5 mg of 3,4-DNT into a 50 mL volumetric flask and diluting to volume with acetonitrile. To prepare the working surrogate spike, 0.5 mL of the stock spike solution is diluted to 100 mL with acetonitrile for a final concentration of 6.25 μg/mL. To each 500 mL aliquot of sample 0.5 mL of the working stock is added.

3.3.3 Stock solutions must be replaced after one year or sooner if degradation of the solution is detected.

3.3.4 Working solutions must be replaced after six months or sooner if degradation of the solution is detected.

3.4 SOLUTION VERIFICATION

3.4.1 Verification of the calibration standards is based on the analysis of daily QC spikes and of independently prepared reference standards.

3.4.2 The daily QC working spike solution will be verified prior to initial use and when samples have not been spiked and the QC are determined to be in control within the previous 7 days.

4.0 SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE

There are no special considerations required due to the nature of explosives. The samples need to be chilled immediately to 4 °C ± 2 °C immediately following sampling.

4.2 STORAGE CONDITIONS

Samples and extracts should be kept chilled to 4 °C ± 2 °C and in the dark.

4.3 HOLDING TIME LIMITS

Samples must be extracted within 7 days of sampling date, and the extract must be analyzed within 40 days of extraction date.

5.0 PROCEDURE

5.1 EXTRACTION

5.1.1 Condition a 6 mL Waters Porapak Rdx Extraction Column by rinsing with 15 mL of acetonitrile and 30 mL of water.

5.1.2 Five hundred milliliters of the sample are measured, spiked with 0.5 mL of the surrogate solution and passed through the column at a rate of 10 mL/minute (Note: Care should be taken to prevent the column from going dry until elution is complete. **DO NOT ALLOW THE COLUMN TO GO DRY**).

5.1.3 The column is then slowly eluted with 3 mL of acetonitrile at a flow rate of no greater than 3 mL/min into a 10 mL volumetric flask. Be sure all of the acetonitrile is blown out of the column.

5.1.4 Dilute the eluate to 10 mL final volume with HPLC water.

5.2 INSTRUMENTAL ANALYSIS

Instrumental analysis involves injection of 500 μL of the extract onto the analytical column described in Section 2.2. The instrumental conditions are specified in Section 2.2 and the integrated output of the UV detector is used in the calculations of Section 6.0. All responses within each analyte's retention window (Section 5.3) which corresponds to concentrations greater than or equal to the respective reporting limit must be confirmed by analysis on a second HPLC column with dissimilar bonded phase material (e.g. CN instead of ODS).

5.2.1 The following analysis sequence will be used when analyzing samples using an initial calibration. Preparation of the standards is described in 3.2.

1. Blank
2. Standard E2
3. Standard E5
4. Standard D
5. Standard D2
6. Standard D5
7. Standard C
8. Standard C2
9. Standard B
10. ICV Standard
11. Method Blank
12. Low Spike
13. High Spike 1
14. High Spike 2
15. Sample Matrix Spike*
16. Sample Matrix Spike Duplicate*
17 Sample(s)
18. Standard B (Post run CCS)

* If required by contract.

5.2.2 The following analysis sequence will be performed when analyzing samples using a daily calibration after initial calibration has previously been performed. If the response of the daily calibration standards is not within $\pm$ 25% of the response of the same standards from the initial daily calibration, then a new initial calibration must be performed.

1. Blank
2. Standard E2
3. Standard D5
4. Standard B
5. Method Blank
6. Low Spike
7. High Spike 1
8. High Spike 2
9. Sample Matrix Spike*
10. Sample Matrix Spike Duplicate*
11. Sample(s)
12. Standard B (Post run CCS)

* If required by contract.

5.3 PEAK IDENTIFICATION

GUIDANCE FOR THE EVALUATION OF CHROMATOGRAMS FOR TARGET ANALYTE DETECTION AND CONFIRMATION

5.3.1 The retention time for an analyte will be determined to be the average retention time of the daily calibration standards that fall within the range of the reporting limit.

5.3.2 If there are no peaks present, then the initial detection is considered to be a non detect. If there are peaks detected in the window, then the chemist will examine the chromatogram to determine if there is indeed a peak present. Matrix noise can cause baseline aberrations and multitudes of peaks in the retention window of interest. If the chemist determines that there is no viable peak in the window, then the peak will be considered a non detect with matrix interference in the retention time window (MI). If the chemist determines that there exists the possibility of a target analyte hit, then the response of the peak is checked against the response of the calibration standard at the reporting limit. If the response of the peak is less than the response of the calibration standard at the reporting limit, it will be labelled as below the detection limit (BDL). If the chemist determines that there exists the possibility of a reportable target analyte hit, then a confirmation analysis is performed and the data are evaluated using the same criteria used for evaluating primary analysis.

5.3.3 The retention windows for the identification of target analytes will be determined on a daily basis using the calibration standards and the continuing calibration standards. Following the evaluation of the data based on retention windows, the use of relative

retention time (RRT) windows will be used for further evaluation of the target analyte determination. The analyst in all cases will have the ability to override the retention windows if they can justify and document that the peak is a target analyte. The following procedure shall be used for the determination of retention windows (RW) and RRT windows:

1. The average retention time (RT) will be determined by calculating the average RT of the daily calibration standards.

2. The standard deviation of the window will be calculated using the RT of the daily calibration standards and the RT of the continuing calibration standards.

3. The RW will be defined as the average RT plus or minus 3 times the standard deviation of the RT for that analyte.

4. The RRT will be calculated by dividing the RT of the analyte by the RT of the surrogate for the same analysis.

5. The average RRT will be calculated using the RRTs of the daily calibration standards.

6. The standard deviation of the RRT will be calculated using the daily calibration and RRT of the continuing calibration standards.

7. The RRT window will be defined as the average RRT plus or minus three times the standard deviation of the RRT.

5.3.4 Based on the above criteria, the following codes shall be used with the appropriate condition:

BDL An analyte was detected but the response is less than the reporting limit. This code can be used on both the primary and the confirmatory column.

MI No viable peak in the area of interest and the response is due to matrix interference. This code can be used on both columns.

NC A peak was detected that met the requirements for being a target analyte but the peak was not confirmed or was BDL on the confirmation analysis. This code should be used on the primary analysis only.

Any peak that is not labelled with a code shall be considered to be confirmed.

5.3.5 Based on a review of the historical data, the guidance window will be set at 0.1 minutes for the chromatographic data system.

5.3.6 The analyst can override the window if sufficient documentation is provided to justify the override.

5.4 CONFIRMATION ANALYSIS

Analytes that are tentatively identified on the primary column must be confirmed by analysis on a different column with a different liquid phase. In order to confirm an analyte, a response must be present in the retention windows for the analyte on both the primary column and the confirmation column. The retention windows will be calculated the same way for both columns. Decision points to be made for the identification and reporting of a target analyte are:

5.4.1 Is there a response in the retention window of a target analyte on the primary column and the response is above the reporting limit (RL)?

No. No further action is necessary and the analyte is reported as <RL.

Yes. Analyze the sample extract on the confirmation column.

5.4.2 Is there a response on the confirmation column in the retention window of the target analyte and the response is above the criterion of detection?

No. The analyte is not confirmed and the analyte is reported as <RL adjusted for any dilutions required.

Yes. Determine ability to identify peak.

5.4.3 Is the peak well defined?

Yes. The analyte is confirmed and the response of the target analyte is reported from the primary column analysis.

No. There is considerable interference on the confirmation column analysis which in the analyst's judgement precludes their ability to identify a peak in the retention window of interest. The analyte is considered as not confirmable. The analyte will be reported with the concentration calculated from the primary column and flagged with a "Q".

5.4.4 The following sequence will be used for the confirmation analysis:

1. Blank
2. Standard E2
3. Standard D5
4. Standard B
5. Method Blank
6. High Spike 1

7. Sample(s)
8. Standard D5

5.5 RETENTION ORDER

The retention order and approximate retention times for the explosive compounds using the certified conditions are:

PRIMARY COLUMN

HMX	5.61 min.
RDX	8.03 min.
135TNB	10.40 min.
13DNB	12.62 min.
TETRYL	13.40 min.
NB	14.08 min.
34DNT	15.49 min.
246TNT	15.76 min.
4A26DT	16.91 min.
2A46DT	17.89 min.
26DNT	18.58 min.
24DNT	19.03 min.
2NT	21.87 min.
4NT	23.31 min.
3NT	25.06 min.

CONFIRMATION COLUMN

NB	8.27 min.
13DNB	9.35 min.
135TNB	9.82 min.
Nitrotoluenes	10.48 min.
26DNT	11.42 min.
24DNT	12.02 min.
246TNT	13.10 min.
4A26DT	13.55 min.
2A46DT	14.65 min.
34DNT (Surr.)	15.12 min.
RDX	17.17 min.
Tetryl	25.50 min.
HMX	32.38 min.

6.0 CALCULATIONS

Linear regression equations are calculated from the initial calibration curve data by regressing the response versus the concentration for each compound. The concentration of a target compound in the sample extract is calculated by substituting the response into the calibration curve equation. The same injection volume is used for standards and sample extracts. The following formula is used to calculate sample concentrations (SC).

$$SC\ (\mu g/L) = \frac{EC \times EV}{SV}$$

Where EC = Extract concentration determined from calibration curve in μg/L.

EV = Extract volume (10 mL).

SV = Sample volume (500 mL).

7.0 DAILY QUALITY CONTROL

7.1 CONTROL SAMPLES

7.1.1 Method blanks will be prepared and analyzed at a frequency of one method blank per lot to verify that the laboratory is not a source of sample contamination.

7.1.2 Standard spikes consisting of all control analytes as defined in section 3.3 will be prepared by spiking into Type II water and analyzed at a frequency of two high spikes and one low spike per lot to verify laboratory performance.

7.1.3 Surrogate spikes as described in section 3.4 will be added to all environmental and QC samples to assess system performance.

7.1.4 Sample matrix spikes will be performed only when requested and at the required frequency based on specific project QA plans. When matrix spikes are prepared they will be spiked with the high spike control sample solution.

7.2 CONTROL CHARTS

Control charts are prepared for the control analytes using the percent recovery data from both the duplicate high level spikes and the low level spike according to the following equation:

$$\text{Percent Recovery} = \frac{\text{Found Concentration}}{\text{Spiked Concentration}} \times 100$$

Preparation of control charts requires the following data:

7.2.1 Accuracy: Two point average percent recovery for the high level spikes within each lot and a three day average of percent recoveries of the low spikes from the previous two lots.

7.2.2 Precision: Two point average difference between the high spike recoveries and the largest difference between the three low recoveries from the previous two lots.

7.2.3 For values that fall outside of the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken. Initial warning and control limits will be established by USAEC using laboratory performance data.

7.2.4 Out-of-control situations to be addressed are specified in section 8.7 of the U.S. Army Environmental Center Guidelines for Implementation of ER-1110-1-263 for USAEC Projects (May 1993).

7.2.5 See Appendix L of U.S. Army Environmental Center Guidelines for Implementation of ER-1110-1-263 for USAEC Projects (May, 1993) for a discussion of modified control limits.

8.0 REFERENCES

U. S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects. May, 1993.

9.0 ATTACHMENTS

ATTACHMENT 1 MDL RESULTS

REPORTING LIMITS AND METHOD DETECTION LIMITS FOR PRIMARY AND CONFIRMATION ANALYSES

Analyte	Reporting Limit (µg/L)	MDL*	MDL**
HMX	0.20	0.056	0.260
RDX	0.20	0.141	0.099
135-TNB	0.10	0.019	0.027
13-DNB	0.10	0.046	0.033
TETRYL	1.00	0.070	0.145
NB	0.10	0.059	0.039
246-TNT	0.10	0.045	0.063
4A26DNT	0.10	0.096	0.087
2A46DNT	0.10	0.043	0.066
26-DNT	0.07	0.034	0.065
24-DNT	0.06	0.016	0.035
2-NT	0.20	0.013	0.123
4-NT	0.20	0.058	0.128
3-NT	0.20	0.057	0.128

* Primary Column

** Confirmation Column

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: DETERMINATION OF EXPLOSIVES IN SOIL BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (METHOD EXL1-S)

TABLE OF CONTENTS

TITLE: DETERMINATION OF EXPLOSIVES IN SOIL BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (METHOD EXL1-S)

1. SUMMARY AND APPLICATION

1.1 SUMMARY

The method involves the extraction of 2 grams of an environmental soil sample using acetonitrile and overnight sonication in an ultrasonic bath. The soil sample is spiked with a a surrogate (3,4-Dinitrotoluene) prior to the extraction. The solvent is decanted and diluted to final volume with water. The compounds are separated by high performance liquid chromatography (HPLC) using isocratic elution and detected using ultraviolet (UV) absorbance at 250 nanometers (nm).

1.2 APPLICATION

1.2.1 This method is applicable to all environmental soil and sediment matrices.

1.2.2 This method is applicable to the Class 1 analysis of the following nitroaromatic and nitramine compounds in environmental soil samples:

Analytes
1,3-Dinitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
HMX (octahydro-1,3,5,7-tetranitro-s-tetrazocine)
Nitrobenzene
RDX (hexahydro-1,3,5-trinitro-s-triazine)
Tetryl (N-methyl-N,2,4,6-tetranitrobenzenamine)
1,3,5-Trinitrobenzene
2,4,6-Trinitrotoluene
4-Amino-2,6-Dinitrotoluene
2-Amino-4,6-Dinitrotoluene
2-Nitrotoluene
3-Nitrotoluene
4-Nitrotoluene

1.2.3 The Chemical Abstract Service (CAS) numbers and the USAEC acronyms for the explosives are presented in Table 1-1.

1.2.4 The reporting limits and lower and upper standard ranges are presented in Table 1-2.

1.2.5 Interferences

1.2.5.1 Any materials which are extracted from soil and coelute with the explosives through the HPLC column, and which absorb ultraviolet radiation at 250 nm may cause interferences. Carryover from analysis of a highly contaminated sample can result in apparent contamination of the succeeding samples analyzed. Such contamination is often manifest by the presence of unusually broad chromatographic peaks nested among narrower peaks. This interference is minimized by analyzing apparent heavily contaminated samples at the end of a run, or running blanks after heavily contaminated samples until carryover is removed, and/or rinsing the system with a mobile phase containing a high proportion of organic modifier until the contamination is removed.

1.2.6 Analysis Rate

1.2.6.1 After instrument calibration, one analyst can analyze approximately 12 samples in an 8-hour day.

1.2.7 Safety Information

1.2.7.1 The target compounds in this method are toxic explosives and some are known carcinogens, e.g. 2,6-Dinitrotoluene. The preparation of all standards should be performed in a laboratory hood. Adequate dermal protection must be used when handling samples and standards. Most of these compounds are either primary or secondary explosives and should be handled with care to avoid contact with electrostatic shocks or impacts. Tetryl and RDX have intermediate sensitivity between initiating explosives and explosives used as bursting

charges. Tetryl is toxic when taken internally or by skin contact. RDX, HMX, and 246TNT are used as bursting charge explosives. Although 246TNT is less sensitive to friction and impact than many other high explosives, it can be detonated with moderate force when confined between metal surfaces such as on the threads of bolts. 246TNT will form sensitive materials in the presence of alkalies.

Table 1-1. USAEC Acronyms and CAS Numbers for Explosives

ANALYTE	ACRONYM	CAS NUMBER
HMX	HMX	2691-41-0
RDX	RDX	121-84-4
1,3,5-Trinitrobenzene	135TNB	25377-32-6
1,3-Dinitrobenzene	13DNB	99-65-01
Tetryl	TETRYL	479-45-8
Nitrobenzene	NB	98-95-3
2,4,6-Trinitrotoluene	246TNT	118-96-7
4-Amino-2,6-Dinitrotoluene	4A26DT	1946-51-0
2-Amino-4,6-Dinitrotoluene	2A46DT	118-96-7
2,6-Dinitrotoluene	26DNT	606-20-2
2,4-Dinitrotoluene	24DNT	121-14-2
2-Nitrotoluene	2NT	88-72-2
4-Nitrotoluene	4NT	99-99-0
3-Nitrotoluene	3NT	99-08-1

Table 1-2. Reporting Limits and Lower and Upper Standard Ranges for Explosives in Soil by Method XXXX-S.

Parameter	Reporting Limit $\mu g/g$	Upper Reporting Limit ($\mu g/g$)	Lower Standard ng/mL	Upper Standard ng/mL
HMX	0.50	20.4	8.16	4080
RDX	0.50	21.0	8.39	4200
1,3,5-Trinitrobenzene	0.25	11.1	4.45	2220
1,3-Dinitrobenzene	0.25	7.4	2.97	1480
Tetryl	0.50	11.3	4.52	2260
Nitrobenzene	0.25	9.25	3.70	1850
2,4,6-Trinitrotoluene	0.25	10.45	4.18	2090
4-Amino-2,6-Dinitrotoluene	0.25	9.1	4.49	2250
2-Amino-4,6-Dinitrotoluene	0.25	11.45	3.65	1820
2,6-Dinitrotoluene	0.20	7.65	4.58	2290
2,4-Dinitrotoluene	0.20	17.1	3.06	1530
2-Nitrotoluene	0.50	23.0	6.84	3420
4-Nitrotoluene	0.50	7.92	9.20	4600
3-Nitrotoluene	0.50	19.8	7.92	3960

2.0 APPARATUS AND CHEMICALS

2.1 GLASSWARE/HARDWARE

2.1.1 Ten milliliter volumetric flasks.

2.1.2 Ultrasonic bath capable of maintaining a temperature of less than 30°C for 18 hours.

2.1.3 Class A Volumetric flasks - 10, 100 and 500 mL.

2.1.4 Class A Volumetric pipets - 0.5, 1.0, 2.0 mL, 3 mL.

2.1.5 Five milliter syringe with 0.45 micron Acrodisc CR filters or equivalent.

2.1.6 Disposable micro pipets - 25, 50, 100 and 200 μL.

2.2 INSTRUMENTATION AND INSTRUMENTAL CONDITIONS

PRIMARY ANALYSIS

2.2.1 HPLC - Shimadzu model SCL-10A HPLC with Shimadzu model SIL-10A autosampler (or equivalent).

2.2.2 Detector: Shimadzu SPD-10A variable wavelength UV detector set at 250 nm.

2.2.3 Column: Phenomenex ODS (octadecylsilane), reverse-phase column, 25 cm length x 4.6 mm I.D., 5 micrometers (μm) particle size (Phenomenex, Inc. Torrance, Ca.).

2.2.4 Mobile phase: Isocratic, 55% methanol/45% water (V/V).

2.2.5 Flow rate: 0.8 mL/min.

2.2.6 Injection volume: 500 μL.

2.2.7 Temperature: Ambient.

CONFIRMATION ANALYSIS

2.2.8 Shimadzu model LC-6A with Shimadzu SIL-6A autosampler or equivalent.

2.2.9 Detector: Shimadzu SPD-6A at 250 nm.

2.2.10 Column: Zorbax Cyano, 250 x 4.6 mm, 5 μm packing.

2.2.11 Mobile phase: Isocratic, 50/50 (v/v) methanol/water.

2.2.12 Flow rate: 1 mL/min..

2.2.13 Injection volume: 500 μL.

2.2.14 Temperature: Ambient.

2.3 CHEMICALS

2.3.1 Methanol (HPLC grade - American Burdick & Jackson, McGaw Park, IL).

2.3.2 Water (ASTM Type II/HPLC grade - American Burdick & Jackson, McGaw Park, IL).

2.3.3 Acetonitrile (HPLC grade - American Burdick & Jackson, McGaw Park, IL).

2.3.4 Acetone (HPLC grade - American Burdick & Jackson, McGaw Park, IL).

2.4 STANDARDS

1. The standards used for target compound certification and calibration are USAEC supplied standard analytical reference materials (SARMS) except for the additional compounds added to the method (2A46DT, 4A26DT, 2NT, 3NT, 4NT and the surrogate 34DNT). Standard materials for the additional compounds were obtained from 2 sources: Aldrich Chemical Co. (2NT, 3NT, 4NT, and 34DNT); and, the Naval Surface Weapons Center -NSWC (2A46DT and 4A26DT). HPLC

characterizations of the non USAEC SARMS showed that only the compounds of interest were present. The USAEC SARMS used for this certification, and their lot numbers are listed below:

Analyte	SARM LOT NUMBER
1,3-Dinitrobenzene	2250
2,4-Dinitrotoluene	1147
2,6-Dinitrotoluene	1148
HMX	1217
Nitrobenzene	2177
RDX	1130
Tetryl	1149
1,3,5-Trinitrobenzene	1154
2,4,6-Trinitrotoluene	1129

3.0 CALIBRATION

Table 3-1 summarizes the concentration of calibration stock solutions and preparation of intermediate calibration standards. Table 3-2 summarizes the preparation and concentration of calibration standards used for initial and daily calibration. To summarize the information presented, individual and separate primary stock solutions (SPSS's) are prepared for each compound by dissolving a known amount of the SARM in 10 or 25 mL of acetonitrile. The nominal concentrations of these SPSS range from 500 to 3500 μg/mL. Two subsets of combined intermediate stock solutions are prepared to prevent degradation due to specific combinations of compounds. These two stock solutions are made up in acetonitrile. The range of concentrations in these two solutions is from 15 - 50 μg/mL. A 10 mL final volume of each calibration standard is prepared by dilution of the stocks to have a 30% acetonitrile concentration to match the acetonitrile concentrations in the final sample extracts.

3.1 INITIAL CALIBRATION

3.1.1 Preparation of Standards

Table 3-1 presents the procedure for preparing separate primary stock solutions, combined intermediate stock solutions and Tetryl calibration standards used for preparation of initial and daily calibrations during actual sample analysis. For initial calibration, Standards E2, E5, D, D2, D5, C, C2,

B and a blank described in Table 3-2 are prepared. These solutions are prepared fresh as needed but not stored for use longer than one month at 4° ± 2 °C (10 mL of standard usually lasts 8 runs). The SPSS are prepared fresh every 12 months and stored in the dark at 4° ± 2 °C. Tetryl needs to be made fresh if degradation is evident but at least every 12 months. Each separate stock solution is made to volume with acetonitrile. The combined intermediate solutions are prepared fresh every 6 months (if 2 separate Stock A solutions are not made, degradation of some compounds may occur). HPLC-grade water is used for dilution to final volumes for the composite calibration standards (acetonitrile concentrations need to be no greater than 30%). Daily calibration standards are E2, D5, B and a blank as outlined in Table 3-2.

3.1.2 Instrument Calibration

3.1.2.1 Inject 500 μL of each calibration standard presented in Table 3-2, and analyze a reference standard following calibration and at the end of the run. Instrument conditions and the column are described in Sec. 2-2.

3.1.3 Independent Reference Standard

Reference materials are available for verification from Accustandard and Crescent Chemicals and are used for verification of the standard curve.

3.1.3.1 The independent reference must be analyzed with the initial calibration run and the results must be within ± 25% of the expected value. If the analysis of the independent reference standard fails, the source of the problem must be identified and corrected. The results of the second analysis of the independent reference standard must be within the acceptable limits before the analysis of samples may proceed. Since a new initial calibration is not performed daily, a reference is required at least weekly.

Table 3-1. Concentration of Primary and Intermediate Stock Solutions

ANALYTE	MASS (mg)	VOLUME (mL)	CONCENTRATION (μg/mL)	Volume (mL)	Final Volume (mL)	Intermediate Stock I Conc. (μg/mL)
HMX	85.0	25	3400	0.3	25	40.80
RDX	43.8	25	1748	0.6	25	41.95
1,3,5-Trinitrobenzene	55.5	25	2224	0.25	25	22.24
1,3-Dinitrobenzene	46.5	25	1856	0.2	25	14.85
2,4-Dinitrotoluene	38.3	25	1528	0.25	25	15.28
Nitrobenzene	115.8	25	4628	0.1	25	18.51
2,4,6-Trinitrotoluene	26.0	25	1044	0.5	25	20.88

ANALYTE	MASS (mg)	VOLUME (mL)	CONCENTRATION (μg/mL)	Volume (mL)	Final Volume (mL)	Intermediate Stock II Conc. (μg/mL)
3,4-Dinitrotoluene*	40.0	25	1598	0.5	25	31.96
4-Amino-2,6-Dinitrotoluene	23.4	25	936	0.6	25	22.46
2-Amino-4,6-Dinitrotoluene	28.5	25	1140	0.4	25	18.24
2,6-Dinitrotoluene	57.3	25	2288	0.25	25	22.88
2-Nitrotoluene	33.0	25	1316	0.65	25	34.22
4-Nitrotoluene	57.5	25	2300	0.5	25	49.00
3-Nitrotoluene	49.5	25	1980	0.5	25	39.60

ANALYTE	MASS (mg)	VOLUME (mL)	CONCENTRATION (μg/mL)	Volume (mL)	Final Volume (mL)	Intermediate Stock Conc. (μg/mL)
Tetryl	56.5	25	2260	0.5	10	113.0

*Surrogate

3.2 DAILY CALIBRATION

3.2.1 Preparation of Standards: Standards E2, E5, D, D2, D5, C, C2, B, and a blank are prepared in 30% Acetonitrile/70% Water from solutions in Table 3-2.

Table 3-2. Preparation of Daily Calibration Standards

Standard	E2	E5	D	D2	D5	C	C2	B
Volume, mL	1.0	0.5	1.0	0.2	0.5	1.0	2.0	1.0 of I and II, 0.2 of Tetryl
Final Volume, mL	10	10	10	10	10	10	10	10
Solution	D2	C	C	B	B	B	B	I, II and Tetryl
HMX	8.16	20.4	40.8	81.6	204	408	816	4080
RDX	8.39	21.0	42.0	83.9	210	420	839	4200
TNB	4.45	11.1	22.2	44.5	111	222	445	2220
DNB	2.97	7.42	14.9	29.7	74.2	149	297	1490
TETRYL	4.52	11.3	22.6	45.2	113	226	452	2260
NB	3.70	9.26	18.5	37.0	92.6	185	370	1851
3,4-DNT	6.39	16.0	32.0	63.9	160	320	639	3200
TNT	4.18	10.4	20.9	41.8	104	209	418	2090
4A26DNT	4.49	11.2	22.5	44.9	112	225	449	225
2A46DNT	3.65	9.12	18.2	36.5	91.2	182	365	1824
26DNT	4.58	11.4	22.9	45.8	114	229	458	2290
24DNT	3.06	7.64	15.3	30.6	76.4	153	306	1530
2NT	6.84	17.1	34.2	68.4	171	342	684	3422
4NT	9.20	23.0	46.0	92.0	230	460	920	4600
3NT	7.92	19.8	39.6	79.2	198	396	792	3960

A* - Prepared from the Intermediate stocks I, II and Tetryl

3.2.2 Daily Instrument Calibration and Calibration Checks

At the beginning of each daily analytical run after initial calibration, inject 500 μL of the three daily calibration standards (5.2.2). Found concentrations are determined from the linear regression equations of initial calibration, therefore the percent recovery (100*Found/Target) must be within 25% of the true value (100%). After every seven lots, a new initial calibration curve is run.

3.2.3 Analysis of Continuing Calibration Data

Continuing calibration will be performed every 12 hours and at the end of the analytical run. The response of the target compounds in the continuing calibration and end run standards (B) must be less than 25 percent different from response factors obtained from Standard B analyzed at the beginning of the day. If the response is greater than 25 percent different, the standard will be reanalyzed. If reanalysis still fails the 25-percent criterion, a new initial calibration must be performed and all analyses since the last acceptable calibration must be repeated.

3.3 DAILY QUALITY CONTROL - Spike Solution Preparation

3.3.1 Control Samples

Daily quality control samples consist of a standard matrix method blank (USAEC standard soil), a single low level spike at approximately twice the reporting limit and duplicate high spikes at 10 times the low spike. These quality control samples should be carried throughout the entire method at the same time samples are run. Table 3-3 documents the preparation of stock spiking solutions and preparation of spiking solutions. Separate Primary Stock Standards (SPSS) at various concentrations are weighed and diluted to 10 mL with acetonitrile as presented in Table 3-3. Each SPSS is diluted to prepare a combined intermediate stock solution for the low and high spikes as presented in Table 3.3. The high spike solution is is prepared by diluting 0.2 mL of each SPSS to 10 mL with acetonitrile. The low spike solution is prepared by diluting 1 mL of the high spike solution to 10 mL with acetonitrile.

Table 3-3. Preparation of Daily Control Spike Solutions

Analyte	Mass (mg)	Vol. (mL)	Conc. mg/mL	High Spike			Low Spike		
				Vol. (mL)	Final (mL)	Conc. µg/mL	Vol. mL	Final mL	Conc., µg/mL
RDX	10	10	1.0	0.2	10	20.0	1	10	2.0
135TNB	5	10	0.5	0.2	10	10.0	1	10	1.0
NB	5	10	0.5	0.2	10	10.0	1	10	1.0
246TNT	5	10	0.5	0.2	10	10.0	1	10	1.0
2A46DT	5	10	0.5	0.2	10	10.0	1	10	1.0
24DNT	4	10	0.4	0.2	10	8.0	1	10	0.8
13DNB	5	10	0.5	0.2	10	10.0	1	10	1.0
2NT	10	10	1.0	0.2	10	20.0	1	10	2.0
3NT	10	10	1.0	0.2	10	20.0	1	10	2.0
4NT	10	10	1.0	0.2	10	20.0	1	10	2.0

1 mL of the spike solutions is added to 2 grams of AEC standard soil to prepare the 2 high and 1 low daily control spike.

Table 3-4. Concentration of Daily Control Spikes

Analyte	Low Spike Target (μg/g)	High Spike Target (μg/g)
RDX	1.0	10.0
135TNB	0.50	5.0
NB	0.50	5.0
246TNT	0.50	5.0
2A46DT	0.50	5.0
24DNT	0.40	4.0
13DNB	0.55	5.0
2NT	1.0	10.0
3NT	1.0	10.0
4NT	1.0	10.0

3.3.2 Surrogate Spike: The surrogate stock spiking solution is prepared by weighing 62.5 mg of 3,4-DNT into a 50 mL volumetric flask and diluting to volume with acetonitrile. To prepare the working surrogate spike, 7.0 mL of the stock spike solution are diluted to 100 mL with acetonitrile for a final concentration of 175 μg/mL. To each 2.0 g aliquot of sample 0.1 mL of the working stock is added.

3.3.3 Stock solutions must be replaced after one year or sooner if degradation of the solution is detected.

3.3.4 Working solutions must be replaced after six months or sooner if degradation of the solution is detected.

3.4 SOLUTION VERIFICATION

3.4.1 Verification of the calibration standards is based on the analysis of daily QC spikes and of independently prepared reference standards.

3.4.2 The daily QC working spike solution will be verified prior to initial use and when samples have not been spiked and the QC are determined to be in control within the previous 7 days.

4.0 SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE

There are no special considerations required due to the nature of explosives. The samples need to be chilled immediately to 4 °C ± 2 °C immediately following sampling.

4.2 STORAGE CONDITIONS

Samples and extracts should be kept chilled to 4 °C ± 2 °C and in the dark.

4.3 HOLDING TIME LIMITS

Samples must be extracted within 7 days of sampling date, and the extract must be analyzed within 40 days of extraction date.

5.0 PROCEDURE

5.1 EXTRACTION

5.1.1 Dry each soil sample (30 g) in a foil dish in a hood overnight or until the soil is dry.

5.1.2 After drying, the soil is carefully crushed to a sandy texture. A 2 g aliquot is transferred to a scintillation vial. Another aliquot is used for percent moisture determination (5.1.6). The sample is then spiked with 0.1 mL of the surrogate solution and allowed to sit for 1 hour. Ten milliliters of acetonitrile are added to the vial and the vial is sealed and vortexed for 60 seconds to mix and disperse the sample.

5.1.3 The vials are placed in an ultrasonic bath and sonicated for 18 hours.

5.1.4 The vials are then centrifuged for 20 minutes at 1500 rpm. Three milliters of the extract are filtered through a 0.45 μm Acrodisc filter into a 10 mL volumetric flask.

5.1.5 Immediately prior to analysis the extract is diluted 10 mL with HPLC water.

5.1.6 Weigh 10 g into a preweighed aluminum weigh boat. Place the sample into an oven and dry overnight at 105 °C. Allow the sample to cool to room temperature in a dessicator and reweigh. The difference in the weight of the sample is the percent moisture content of the air dried sample.

5.2 INSTRUMENTAL ANALYSIS

Instrumental analysis involves injection of 500 μL of the extract onto the analytical column described in Section 2.2. The instrumental conditions are specified in Section 2.2 and the integrated output of the UV detector is used in the calculations of Section 6.0. All responses within each analyte's retention window (Section 5.3) which corresponds to concentrations greater than or equal to the respective reporting limit must be confirmed by analysis on a second HPLC column with dissimilar bonded phase material (e.g. CN instead of ODS).

5.2.1 The following analysis sequence will be used when analyzing samples using an initial calibration. Preparation of the standards is described in 3.2.

1. Blank
2. Standard E2
3. Standard E5
4. Standard D
5. Standard D2
6. Standard D5
7. Standard C
8. Standard C2
9. Standard B
10. ICV Standard
11. Method Blank
12. Low Spike
13. High Spike 1
14. High Spike 2
15. Sample Matrix Spike*
16. Sample Matrix Spike Duplicate*
17 Sample(s)
18. Standard B (Post run CCS)

* If required by contract.

5.2.2 The following analysis sequence will be performed when analyzing samples using a daily calibration after initial calibration has previously been performed. If the response of the daily calibration standards is not within $\pm$ 25% of the response of the same standards from the initial daily calibration, then a new initial calibration must be performed.

1. Blank
2. Standard E2
3. Standard D5
4. Standard B
5. Method Blank
6. Low Spike
7. High Spike 1
8. High Spike 2
9. Sample Matrix Spike*
10. Sample Matrix Spike Duplicate*
11. Sample(s)
12. Standard B (Post run CCS)

* If required by contract.

5.3 PEAK IDENTIFICATION

GUIDANCE FOR THE EVALUATION OF CHROMATOGRAMS FOR TARGET ANALYTE DETECTION AND CONFIRMATION

5.3.1 The retention time for an analyte will be determined to be the average retention time of the daily calibration standards that fall within the range of the reporting limit.

5.3.2 If there are no peaks present, then the initial detection is considered to be a non detect. If there are peaks detected in the window, then the chemist will examine the chromatogram to determine if there is indeed a peak present. Matrix noise can cause baseline aberrations and multitudes of peaks in the retention window of interest. If the chemist determines that there is no viable peak in the window, then the peak will be considered a non detect with matrix interference in the retention time window (MI). If the chemist determines that there exists the possibility of a target analyte hit, then the response of the peak is checked against the response of the calibration standard at the reporting limit. If the response of the peak is less than the response of the calibration standard at the reporting limit, it will be labelled as below the detection limit (BDL). If the chemist determines that there exists the possibility of a

reportable target analyte hit, then a confirmation analysis is performed and the data are evaluated using the same criteria used for evaluating primary analysis.

5.3.3 The retention windows for the identification of target analytes will be determined on a daily basis using the calibration standards and the continuing calibration standards. Following the evaluation of the data based on retention windows, the use of relative retention time (RRT) windows will be used for further evaluation of the target analyte determination. The analyst in all cases will have the ability to override the retention windows if they can justify and document that the peak is a target analyte. The following procedure shall be used for the determination of retention windows (RW) and RRT windows:

1. The average retention time (RT) will be determined by calculating the average RT of the daily calibration standards.

2. The standard deviation of the window will be calculated using the RT of the daily calibration standards and the RT of the continuing calibration standards.

3. The RW will be defined as the average RT plus or minus 3 times the standard deviation of the RT for that analyte.

4. The RRT will be calculated by dividing the RT of the analyte by the RT of the surrogate for the same analysis.

5. The average RRT will be calculated using the RRTs of the daily calibration standards.

6. The standard deviation of the RRT will be calculated using the daily calibration and RRT of the continuing calibration standards.

7. The RRT window will be defined as the average RRT plus or minus three times the standard deviation of the RRT.

5.3.4 Based on the above criteria, the following codes shall be used with the appropriate condition:

BDL An analyte was detected but the response is less than the reporting limit. This code can be used on both the primary and the confirmatory column.

MI No viable peak in the area of interest and the response is due to matrix interference. This code can be used on both columns.

NC A peak was detected that met the requirements for being a target analyte but the peak was not confirmed or was BDL on the confirmation analysis. This code should be used on the primary analysis only.

Any peak that is not labelled with a code shall be considered to be confirmed.

5.3.5 Based on a review of the historical data, the guidance window will be set at 0.1 minutes for the chromatographic data system.

5.3.6 The analyst can override the window if sufficient documentation is provided to justify the override.

5.4 CONFIRMATION ANALYSIS

Analytes that are tentatively identified on the primary column must be confirmed by analysis on a different column with a different liquid phase. In order to confirm an analyte, a response must be present in the retention windows for the analyte on both the primary column and the confirmation column. The retention windows will be calculated the same way for both columns. Decision points to be made for the identification and reporting of a target analyte are:

5.4.1 Is there a response in the retention window of a target analyte on the primary column and the response is above the reporting limit (RL)?

No. No further action is necessary and the analyte is reported as <RL.

Yes. Analyze the sample extract on the confirmation column.

5.4.2 Is there a response on the confirmation column in the retention window of the target analyte and the response is above the criterion of detection?

No. The analyte is not confirmed and the analyte is reported as <RL adjusted for any dilutions required.

Yes. Determine ability to identify peak.

5.4.3 Is the peak well defined?

Yes. The analyte is confirmed and the response of the target analyte is reported from the primary column analysis.

No. There is considerable interference on the confirmation column analysis which in the analyst's judgement precludes their ability to identify a peak in the retention window of interest. The analyte is considered as not confirmable. The analyte will be reported with the concentration calculated from the primary column and flagged with a "Q."

5.4.4 The following sequence will be used for the confirmation analysis:

1. Blank
2. Standard E2
3. Standard D5
4. Standard B
5. Method Blank
6. High Spike 1
7. Sample(s)
8. Standard D5

5.5 RETENTION ORDER

The retention order and approximate retention times for the explosives using the described conditions are:

PRIMARY COLUMN

HMX	5.61 min.
RDX	8.03 min.
135TNB	10.40 min.
13DNB	12.62 min.
TETRYL	13.40 min.
NB	14.08 min.
34DNT	15.49 min.
246TNT	15.76 min.
4A26DT	16.91 min.
2A46DT	17.89 min.
26DNT	18.58 min.
24DNT	19.03 min.
2NT	21.87 min.
4NT	23.31 min.
3NT	25.06 min.

CONFIRMATION COLUMN

NB	8.27 min.
13DNB	9.35 min.
135TNB	9.82 min.
Nitrotoluenes	10.48 min.
26DNT	11.42 min.
24DNT	12.02 min.
246TNT	13.10 min.
4A26DT	13.55 min.
2A46DT	14.65 min.
34DNT	15.12 min.

RDX	17.17 min.
Tetryl	25.50 min.
HMX	32.38 min.

6.0 CALCULATIONS

Linear regression equations are calculated from the initial calibration curve data by regressing the response versus the concentration for each compound. The concentration of a target compound in the sample extract is calculated by substituting the response into the calibration curve equation. The same injection volume is used for standards and sample extracts. The following formula is used to calculate sample concentrations (SC).

$$SC\ (\mu g/g) = \frac{EC \times EV}{SW}$$

Where EC = Extract concentration determined from calibration curve in μg/mL.

EV = Extract volume (30 mL).

SW = Sample weight (2 g).

7.0 DAILY QUALITY CONTROL

7.1 CONTROL SAMPLES

7.1.1 Method blanks will be prepared and analyzed at a frequency of one method blank per lot to verify that the laboratory is not a source of sample contamination.

7.1.2 Standard spikes consisting of all control analytes as defined in section 3.3 will be prepared by spiking into Type II water and analyzed at a frequency of two high spikes and one low spike per lot to verify laboratory performance.

7.1.3 Surrogate spikes as described in section 3.4 will be added to all environmental and QC samples to assess system performance.

7.1.4 Sample matrix spikes will be performed only when requested and at the required frequency based on specific project QA plans. When matrix spikes are prepared they will be spiked with the high spike control sample solution.

7.2 CONTROL CHARTS

Control charts are prepared for the control analytes using the percent recovery data from both the duplicate high level spikes and the low level spike according to the following equation:

$$\text{Percent Recovery} = \frac{\text{Found Concentration}}{\text{Spiked Concentration}} \times 100$$

Preparation of control charts requires the following data:

7.2.1 Accuracy: Two point average percent recovery for the high level spikes within each lot and a three day average of percent recoveries of the low spikes from the previous two lots.

7.2.2 Precision: Two point average difference between the high spike recoveries and the largest difference between the three low recoveries from the previous two lots.

7.2.3 For values that fall outside of the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken. Initial warning and control limits will be established by USAEC using laboratory performance data.

7.2.4 Out-of-control situations to be addressed are specified in section 8.7 of the U.S. Army Environmental Center Guidelines for Implementation of ER-1110-1-263 for USAEC Projects (May 1993).

7.2.5 See Appendix L of U.S. Army Environmental Center Guidelines for Implementation of ER-1110-1-263 for USAEC Projects (May, 1993) for a discussion of modified control limits.

8.0 REFERENCES

U. S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects. May, 1993.

9.0 ATTACHMENTS

ATTACHMENT 1 MDL RESULTS

REPORTING LIMITS AND METHOD DETECTION LIMITS FOR PRIMARY AND CONFIRMATION ANALYSES

Analyte	Reporting Limit (μg/g)	MDL*	MDL**
HMX	0.50	0.032	0.203
RDX	0.50	0.192	0.210
135-TNB	0.25	0.050	0.058
13-DNB	0.25	0.010	0.061
TETRYL	0.50	0.297	0.237
NB	0.25	0.108	0.084
246-TNT	0.25	0.039	0.056
4A26DNT	0.25	0.199	0.030
2A46DNT	0.25	0.046	0.019
26-DNT	0.20	0.026	0.063
24-DNT	0.20	0.025	0.106
2-NT	0.50	0.077	0.162
4-NT	0.50	0.174	0.131
3-NT	0.50	0.068	0.128

* Primary Column
** Confirmation Column

METALS BY ICAP
(USAEC METHOD ICP1)

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **DETERMINATION OF METALS IN WATER BY INDUCTIVELY COUPLED ARGON PLASMA SPECTROSCOPY (SW-846/3005/6010) USAEC METHOD - ICP1 - WATER**

TABLE OF CONTENTS

TITLE: DETERMINATION OF METALS IN WATER BY INDUCTIVELY COUPLED ARGON PLASMA SPECTROSCOPY (SW-846/3005/6010)
USAEC METHOD - ICP1 - WATER

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This ESE standard operating procedure follows EPA SW-846 protocols with additional quality control requirements applicable for the Class 1 analysis under the USAEC guidelines for implementation of ER 1110-1-263 of the following elements in environmental water and TCLP digestate samples:

Element	Chemical Symbol
Silver	Ag
Aluminum	Al
Arsenic	As
Boron	B
Barium	Ba
Beryllium	Be
Calcium	Ca
Cadmium	Cd
Cobalt	Co
Chromium	Cr
Copper	Cu
Iron	Fe
Potassium	K
Magnesium	Mg
Manganese	Mn
Molybdenum	Mo
Sodium	Na
Nickel	Ni
Lead	Pb
Antimony	Sb
Selenium	Se
Tin	Sn
Thallium	Tl
Vanadium	V
Zinc	Zn

1.2 GENERAL METHOD

This method employs an acid digestion (using Nitric - HNO3 and Hydrochloric - HCl acid) of a water (SW-846 Method 3005) followed by analysis of the digestate by simultaneous inductively coupled argon plasma (ICP) spectroscopy (SW-846 Method 6010). This method is equivalent to the SW-846 methods except that the water digestion uses a 50 mL sample aliquot instead of a 100 mL aliquot. In addition, the final acid concentration for sample digestates, standards and quality control is 5% (v/v) HNO3 and 5% (v/v) HCl. These modifications are minor to the spirit of the SW-846 methods because digestates have been adjusted after digestion and prior to returning to final digestate volume and matrix matching of standards and samples is considered acceptable laboratory practice for avoiding matrix biases.

Additional quality control samples required by USAEC have been added to the SW-846 requirements: 1) primarily daily control spikes - one spike at two times the reporting limit and two spikes at twenty times the reporting limit; and 2) initial calibration requirements must cover the range of the reporting limit and the upper range where no dilution is required. The following analytes are typically analyzed by this method for the following analytical requests:

EPA TAL List	EPA PP List	TCLP List
Al	Be	As
Ba	Cd	Se
Be	Cr	Ag
Ca	Cu	Pb
Cd	Ni	Cr
Co	Zn	Ba
Cr		Cd
Cu	Ag*	
Fe	Tl*	
K	Pb*	
Mg		
Mn		
Na		
Ni		
V		
Zn		
Ag*		
Pb*		
Tl*		
Sb*		

* These analytes are analyzed by ICP unless GFAA methods are specifically required.

1.3 REPORTING LIMITS AND INITIAL CALIBRATION RANGES - WATERS

MDL studies are performed quarterly to confirm the validity of the chosen reporting limits following the procedure outlined in 40CFR Volume 4 No. 136, Appendix B. Initial calibration must cover the entire range from the reporting limit to the upper range beyond which dilutions are required. The method detection limits, and upper and lower initial calibration standard range for ICAP Metals in Water - Method 3005/6010 are as follows:

Parameter	Reporting Limit (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)
Aluminum	40.0	40.0	1,000,000
Antimony	50.0	50.0	100,000
Arsenic	100	100	100,000
Barium	25.0	25.0	100,000
Beryllium	5.0	5.0	100,000
Boron	50.0	50.0	100,000
Cadmium	5.0	5.0	100,000
Calcium	100	100	1,000,000
Chromium	10.0	10.0	100,000
Cobalt	20.0	20.0	100,000
Copper	5.0	5.0	100,000
Iron	45.0	45.0	1,000,000
Lead	50.0	50.0	100,000
Magnesium	50.0	50.0	1,000,000
Manganese	5.0	5.0	100,000
Molybdenum	10.0	10.0	100,000
Nickel	15.0	15.0	100,000
Potassium	550	550	1,000,000
Selenium	100	100	100,000
Silver	5.0	5.0	100,000
Sodium	100	100	500,000
Thallium	100	100	100,000
Tin	50	50	100,000
Vanadium	10.0	10.0	100,000
Zinc	20.0	20.0	100,000

1.4 INTERFERENCES

Broadly defined, an interference is any unwanted radiation that reaches the photomultiplier tubes. It can arise from background continuum or as true spectral interferences. Sources of background continuum are black-body radiation, bremsstrahlung radiation, and recombination phenomena. These are compensated for by spectrum shifting," i.e., measuring emission intensity on both sides of each analytical line. The average radiation detected "off-center" is subtracted from the intensity measurement taken at the analytical line. Spectral interferences occur when the wavelength separation of the emission lines is less than the spectral bandpass of the detector. By determining the ratio of interfering element to affected element, the computer is programmed to discount the unwanted radiation. These interelement corrections are usually small for water samples. Iron, for example, will give rise to a false signal for cadmium, but the ratio is less than 1:1,000. Magnesium interferes with chromium, but again the effect is quite small. No major interferences were encountered during the documentation of this method. Interelemental correction factors were applied when using the simultaneous instrument.

1.5 ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 35 samples in an 8-hour day. Approximately 35 samples can be digested in an 8-hour day.

1.6 SAFETY INFORMATION

This method involves digestion of aqueous samples with a mixture of nitric acid and hydrochloric acid. Both of these reagents are corrosive and adequate dermal and eye protection are required. Sample digestions should be carried out in a hood with adequate ventilation.

2.0 APPARATUS AND CHEMICALS

2.1 GLASSWARE/HARDWARE

2.1.1 Analytical balance - capable of accurately weighing 0.1 mg;

2.1.2 Griffin beakers or erlenmeyer flasks (150 mL);

2.1.3 Watch glasses or erlenmeyer covers;

2.1.4 Filter funnels and Whatman No. 41 filter paper, or equivalent;

2.1.5 Graduated cylinders (50 mL and 100 mL);

2.1.6 Electric hotplate adjustable and capable of maintaining 90-95°C.

2.1.7 Class A volumetric pipet (10, 5-mL);

2.1.8 Adjustable Eppendorf or equivalent micropipettor (100 and 1000 uL);

2.1.9 Disposable beakers (10-mL).

2.1.10 Class A volumetric flasks (1000, 500, 200, 100, and 10 mL).

2.1.11 Class A volumetric pipettes.

2.1.12 Automatic pipetter, Repipet[R] or equivalent.

2.2 INSTRUMENTATION

2.2.1 Jarrell-Ash 1100(J.A. 1100) Series Mark III Plasma AtomComp Spectrometer or Jarrell-Ash 61E(J.A.61E) equipped with spectrum shifter for background correction. The approximate instrument settings are as follows:

a) Incident RF power - 1.05 kilowatts (kw),

b) Reflected RF power - minimized (<3 kW),

c) Observation height - 20 mm above coil,

d) Sample argon flow rate - 0.5 L/min, and

e) Coolant argon flow rate - 20 L/min.

NOTE: Daily instrument settings may vary due to environmental conditions and the nature of the samples being analyzed. Check solutions and daily control spikes will verify the instrument optimization.

2.3 CHEMICALS AND REAGENTS

2.3.1 Ultra pure concentrated nitric acid and hydrochloric acid.

2.3.2 Stock solutions are purchased for preparing calibration, spiking, reference, and interference check solutions. Solutions must be traceable to NIST standard reference material (vendors include could be Inorganic Ventures, Inc.; High Purity, Inc.; SPEX Industries, Inc. and Perkin Elmer).

2.3.3 The water used for dilution of standards, certification spiking, sample preparation and analysis is ASTM Type I grade (American Society for Testing Materials, Philadelphia, PA.).

2.3.4 Hydrogen peroxide (H2O2); 30%, trace metals grade, Fisher or equivalent distributer.

2.4 ANALYTES

The Chemical Abstract Service (CAS) registry numbers and instrumental wavelengths are as follows and are element specific:

Analyte	CAS Registry Number	Operating Wavelength (nm) J.A. 1100	J.A. 61E
Ag	7440-22-4	328.0	328.0
Al	7429-90-5	308.2	308.2
As	7440-38-2	193.6	193.6
B	7440-42-8	249.7	249.7
Ba	7440-39-3	493.4	493.4
Be	7740-41-77	234.8	313.0
Ca	7440-70-2	317.9	317.9
Cd	7740-43-9	228.8	228.8
Co	7440-48-4	228.6	228.6
Cr	7440-47-3	267.7	267.7
Cu	7440-50-8	324.7	324.7
Fe	7339-89-6	259.9	259.9
K	7440-09-7	766.5	766.5
Mg	7439-95-4	277.0	279.0
Mn	7439-96-5	257.6	257.6
Mo	7439-98-7	202.0	202.0
Na	7440-23-5	589.0	589.0
Ni	7740-02-0	231.6	231.6
Pb	7439-92-1	220.3	220.3
Sb	7740-36-0	217.5	206.8
Se	7782-49-2	196.0	196.0
Tl	7740-28-0	190.8	190.8
V	7440-62-2	292.4	292.4
Zn	7740-66-6	213.8	213.8

3.0 CALIBRATION

3.1 INITIAL CALIBRATION

An initial calibration will be performed after any of the following:

* Major instrument maintenance;
* Instrument modification;
* Replacement of the torch;
* Replacement of the mirror, or
* The daily calibration slope is not within the acceptance criteria of $\pm$ 10 % of the last initial calibration slope.

When initial calibration is required, a minimum of five standards for each element will be analyzed. The standards will consist of a blank, a standard at the reporting limit, two intermediate standards (the daily calibration level and a 1:1 dilution of the daily calibration level) and a standard at the upper linear range. A standard curve will be constructed for each element by plotting the measured response versus the known concentration. The best-fit linear regression line obtained for each metal must have a correlation coefficient (CC) of 0.995 or higher. If the CC is less than 0.995 for any element, the standards for that element must be prepared again and/or a lower upper range standard must be used.

Table 3.1-1 defines and summarizes the preparation of the required initial calibration standards. Table 3.1-1 alsopresents the water reporting limits for comparison to the MDL-1 solution. Dilutions of the MDL-1 solution are prepared to meet MDLs for all elements for initial calibration. The WMDL-1 solution is used for MDL studies and is prepared with 20 % HCL to lengthen the life of the solution (especially for Ag). All solutions injected have an acid concentration of 5% (v/v) HCl and 5% (v/v) HNO3.

The solutions listed in Table 3.1-1 are named and defined as follows

URS-x = Upper range standard with x representing a solution containing certain elements.
MRS-x = Mid range standard with x representing a solution containing certain elements.
MRS.5-x = A 1:1 dilution of the MRS with x representing a solution containing certain elements.
WMDL-1 = Working method detection limit standard stock.
MDL-1 = Method detection limit standard.

Table III-1. Preparation Scheme for Initial Calibration Standards.

	STOCK CONC. mg/L	UPPER RANGE STANDARD ID	MLS STOCK USED (10 ml FINAL VOLUME) mL	FINAL CONC. UPPER RANGE STD. mg/L	MID RANGE STD ID	MLS STOCK USED (1 L FINAL VOLUME) mL	FINAL CONC. MID RANGE STD. mg/L	1:1 MID RANGE STANDARD ID	ML MRS USED (50 mL FINAL VOLUME) mL	FINAL CONC 1:1 MID RANGE STD. mg/L	WORKING MDL STOCK ID	ML STOCK USED (100 mL FINAL VOLUME mL	CONC WORKING MDL STOCK mg/L	MDL STD ID	CONC MDL STD 1:100 OF WMDL-1 ug/L	WATER MDL** ug/L
As	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	1.0	10	MDL-1	100	100
B	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.5	5.0	MDL-1	50	50
Ba	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.05	0.5	MDL-1	5.0	25
Be	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.05	0.5	MDL-1	5.0	5.0
Cd	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.1	1.0	MDL-1	10	5.0
Co	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.3	3.0	MDL-1	30	20
Cr	1000	URS-2	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.2	2.0	MDL-1	20	10
Cu	1000	URS-2	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.1	1.0	MDL-1	10	5.0
Mn	1000	URS-2	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.05	0.5	MDL-1	5.0	5.0
Ni	1000	URS-2	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.5	5.0	MDL-1	50	15
Pb	1000	URS-2	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	1.0	10	MDL-1	100	50
Sb	1000	URS-3	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	1.0	10	MDL-1	100	100
Se	1000	URS-3	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	1.5	15	MDL-1	150	100
Tl	1000	URS-3	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	2.0	20	MDL-1	200	100
V	1000	URS-3	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.15	1.5	MDL-1	15	10
Zn	1000	URS-3	1.0	100	MRS-1	1.0	1.0	MRS 5-1	25	0.5	WMDL-1	0.1	1.0	MDL-1	10	20
Al	10000	URS-4	1.0	1000	MRS-2	1.0	10.0	MRS 5-2	25	5.0	WMDL-1	0.1	10	MDL-1	100	40
Ca	10000	URS-4	1.0	1000	MRS-2	1.0	10.0	MRS 5-2	25	5.0	WMDL-1	0.1	10	MDL-1	100	100
Fe	10000	URS-4	1.0	1000	MRS-2	1.0	10.0	MRS 5-2	25	5.0	WMDL-1	0.05	5.0	MDL-1	50	45
K	10000	URS-4	1.0	1000	MRS-2	10.0	100	MRS 5-2	25	50	WMDL-1	1.5	150	MDL-1	1500	550
Mg	10000	URS-4	1.0	1000	MRS-2	1.0	10.0	MRS 5-2	25	5.0	WMDL-1	0.1	10	MDL-1	100	50
Na	10000	URS-5	1.0	1000	MRS-2	1.0	10.0	MRS 5-2	25	5.0	WMDL-1	0.2	20	MDL-1	200	100
Ag	1000	URS-5	1.0	100	MRS-3	1.0	1.0	MRS 5-3	25	0.5	WMDL-1	0.15	1.5	MDL-1	15	5.0
Mo	1000	URS-5	1.0	100	MRS-3	1.0	1.0	MRS 5-3	25	0.5	WMDL-1	0.15	1.5	MDL-1	15	10
Sn	1000	URS-5	1.0	100	MRS-3	1.0	1.0	MRS 5-3	25	0.5	WMDL-1	1.0	10	MDL-1	100	50

NOTES: All solutions for instrument are made up for 5% (v/v) HNO_3 5% (v/v) HCl. The WMDL-1 Solution is made up for 20 % (v/v) HCL. Dilutions of MDL-1 are prepared to meet all reporting limits.

** The water MDL column is provided for reference to show which compounds will require a dilution of the MDL-1 standard in order to ensure that the initial calibration curve includes a standard at or below the reporting limit.

3.2 DAILY CALIBRATION

3.2.1 Preparation of Daily Calibration Solutions:

All standards and check solution preps are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date. Table 3.2-1 is presented as a summary and guide for preparation as discussed below. All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3 and 5% (v/v) HCl. In addition, different stock solutions should be used for preparation of the calibration standards, CCV, ICVs and the digestion spike solution. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst.

Mixed calibration standards are made by pipetting the appropriate (see Table 3.2-1) volume of each stock solution into a 1000 mL volumetric flask containing approximately 500 mL of Type II water, 50 mL of concentrated HNO_3 and 50 mL of concentrated HCl. The final volume is adjusted to 1000 mL with Type II water. Standard 1 (STD-1) is a calibration blank containing 5% (v/v) HNO_3 and 5% (v/v) HCl. The other solutions are named STD-2 through STD-5. These solutions expire in 33 days.

The continuing calibration verification solution (CCV-1) is prepared by adding the appropriate volume (see also Table 3.2-1) of stock standards to a 1000 mL volumetric flask containing 500 mL Type II water, 50 mL conc. HNO_3 and 50 mL conc. HCl. The final volume is adjusted to 1000 mL with deionized water. The CCV expires in 33 days.

Two multi-element initial calibration verification solution(s) (ICV) are prepared according to the manufacturer's instructions (see also Table 3.2-1). For SPEX reference solutions, 1.0 mL of the stock solution is added to a 100 mL volumetric flask containing 50 mL Type II water, 5 mL conc. HNO_3 and 5 mL conc. HCL. The final volumes are adjusted to 100 mL with Type II water. If an independent reference is not available, the ICV may be prepared from different stock solutions (manufacturer or lot number) than those used to prepare the calibration standards. The elemental concentrations of the ICV are prepared so that they are within the calibration range of the instrument but at concentrations other than those used for instrument calibration. Elemental concentrations for the SPEX solutions are listed in Table 3.2-1. The prepared ICV solutions (ICV-7 and ICV-19) expire in 33 days.

Two multi-element interference check solutions (ICS) are prepared (see also Table 3.2-1) by adding the appropriate volume of stock PE-PURE multi-element CLP solutions to 100 mL volumetric flasks containing approximately 50 mL of Type II water, 5 mL of concentrated HNO_3, and 5 mL of concentrated HCl. ICS-A is prepared with 10 mL of solution A. ICS-B is prepared with 10 mL of solution A and 1 mL of solution B. Final volumes are adjusted to 100 mL with Type II water. The elemental concentrations of each solution are listed in Table 3.2-1. These solutions (ICS-A and ICS-AB) expire in 33 days.

The initial calibration blank (ICB) and continuing calibration blanks (CCB) are acidified deionized water (5% HNO_3 plus 5% HCl). This solution expires in 33 days.

Table 3.2-1. Preparation of Daily Calibration Standards and Check Solutions

ANALYTE		CALIBRATION STANDARDS		CONT. CALIB. VERIFICATION		INITIAL CALIB. VERIFICATION		INTERFERENCE CHECK SOLUTION					
	STOCK CONC. (mg/L)	STANDARD ID	VOLUME OF STOCK USED (mL)	STANDARD CONC. (mg/L)	CCV ID	VOLUME OF STOCK USED (mL)	CCV CONC. (mg/L)	ICV ID	STOCK CONC. (mg/L)	ICV CONC. (mg/L)	ICS ID	STOCKICS CONC. (mg/L)	CONC. (mg/L)
As	1,000	STD-2	1.0	1.0	CCV-1	0.7	0.7	ICV-19	100	1.0	--	--	--
Ba	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-7	100	1.0	ICS-AB	50	0.5
Be	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Cd	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	100	1.0
Co	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Cr	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Cu	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Mn	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Ni	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	100	1.0
Pb	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	100	1.0
Sb	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	--	--	--
Se	1,000	STD-2	1.0	1.0	CCV-1	0.7	0.7	ICV-19	100	1.0	--	--	--
Tl	1,000	STD-2	1.0	1.0	CCV-1	0.7	0.7	ICV-19	100	1.0	--	--	--
V	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Zn	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	100	1.0
Al	10,000	STD-3	1.0	10.0	CCV-1	0.5	5.0	ICV-7	100	1.0	ICS-A	5000	500
Ca	10,000	STD-3	1.0	10.0	CCV-1	0.5	5.0	ICV-19	100	1.0	ICS-A	5000	500
Fe	10,000	STD-3	1.0	10.0	CCV-1	0.5	5.0	ICV-19	100	1.0	ICS-A	2000	200
K	10,000	STD-3	10.0	100.0	CCV-1	0.5	5.0	ICV-7	1000	10.0	--	--	--
Mg	10,000	STD-3	1.0	10.0	CCV-1	0.5	5.0	ICV-19	100	1.0	ICS-A	5000	500
Na	10,000	STD-3	1.0	10.0	CCV-1	0.5	5.0	ICV-7	100	1.0	--	--	--
Ag	1,000	STD-4	1.0	1.0	CCV-1	0.5	0.5	ICV-7	100	1.0	ICS-AB	100	1.0
Mo	1,000	STD-5	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	--	--	--

Notes: STD-1 is the Calibration Blank. All solutions are made to a final acid concentration of 5% (v/v) HCl and 5% (v/v) HNO_3.
STD and CCV solutions are made to final volumes of 1000 mL; ICV and ICS are made to a final volume of 100 mL.

3.2.2 Analysis of Calibration Standards and QC for Daily Calibration:

3.2.2.1 Instrument Daily start-up procedures:

3.2.2.1.1 Check the Argon tank level. The regulator should read approximately 80 ps Turn on the water recirculator, computer, monitor, printer buffer box and printer. Install new peristaltic pump tubing daily and engage.

3.2.2.1.2 Open the coolant and sample valves on the front of the instrument. Aspirate deionized water for approximately 3 minutes watching for even flow through the tubing. Check capillary tubing for kinks or dust balls, replace or remov as necessary. Check the nebulizer for a fine even cloud. If clogged, remov the capillary tubing and spray canned air through the nebulizer. The nebuliz flow should be approximately 0.3 LPM.

3.2.2.1.3 Inspect the torch injector tip for fire polish or salt deposits. If necessary, remove and dip (not soak) the injector tip in 1+1 HF for 2-3 minutes. Rins with water and reinstall. Replace the torch if it is chipped or uneven at the orifice. Note: if the torch is replaced, the torch height must be optimized.

3.2.2.1.4 Inspect the D2 mirror with a flashlight for dust or film. Dust may be blown off with canned air. If the mirror has a film, remove it being careful not to touch the face of the mirror. Clean by rinsing with isopropyl alcohol and th bottled distilled water. Dry completely with canned air and reinstall the mirror. Replace the mirror if it cannot be properly cleaned. Note: if the mirror is replaced, the torch height must be optimized.

3.2.2.1.5 Check the drain bucket and, if necessary, pour out some of the contents, but do not empty below the line indicated on the bucket. Also empty the dehumidifier bucket.

3.2.2.1.6 After aspirating deionized water for a few minutes, close the sample valve an turn on the RF power. When the mass flow of the nebulizer drops near zero turn the power control knob clockwise until the forward power reads 0.5 kw Ignite the torch by pressing the ignitor button briefly and increase the forwar power to 1.25 kw. Open the sample flow valve. Switch on the automatic forward power control and turn the power control knob clockwise until it stops.

3.2.2.1.7 Turn on the reflected power alarm. Reflected RF power meter should read 5 watts or less.

3.2.2.1.8 The instrument should warm up for at least one hour to become thermally stable before beginning plasma optimization and tuning and/or calibration. Room conditions should be between 72 and 78 °F and not exceed 80% humidity.

3.2.2.2 Daily optimation and tuning:

3.2.2.2.1 Enter the PROFILE instrument mode. Aspirate a 5 ppm Cd solution and follow the "manual" directions on the screen. Check PROFILE setting by "automatic" profile. The peak position should be less than 0.1. If the peak position is greater than 0.1, see the Troubleshooting section. Profiling shoul be performed prior to standardization and every four hours to minimize drift

3.2.2.2.2 Enter the ANALYSIS mode. Aspirate a 5 ppm Cu/Mn solution and read 10 replicates. If necessary, adjust the nebulizer mass flow control to approach $\pm$ 2% of the target ratio of Cu to Mn. If the ratio is greater than 2% of the target ratio, see the Troubleshooting section. Note: a new target ratio is determined each time IECs are recalculated.

3.2.2.2.3 The instrument is now ready for calibration and sample analysis.

3.2.2.3 Daily Calibration and analysis of calibration QC:

3.2.2.3.1 An initial calibration will be performed after major instrument maintenance, instrument modification, replacement of the torch and/or mirror, or the daily calibration slope is not within acceptance criteria. See section 3.1 for preparation of initial calibration solutions.

3.2.2.3.2 A daily 2-point calibration will be performed for each element with a blank and a standard at the concentration indicated in the Table 3.2-1 (STD-x solutions). If the slope for any element is not within 10% of the slope calculated during initial calibration, the instrument is recalibrated. If the slo still fails criteria, initial calibration will be performed.

3.2.2.3.3 Reanalyze the standards used in the calibration. The concentration values m be within 5% of their respective true values or the analysis must be terminated, the problem corrected and the instrument recalibrated.

3.2.2.3.4 Flush the system with the calibration blank for at least one minute before the analysis of each sample.

3.2.2.3.5 Initial calibration verification solution(s) must be analyzed after calibration a before any samples are analyzed. All values must be within 10% of their respective true values or the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified prior to sample analyses.

3.2.2.3.6 The interference check solutions are analyzed at the beginning and end of ea sample analysis run. Results must fall within 20% of the true value. If not, terminate the analysis, correct the problem, recalibrate, reverify the calibration, and reanalyze the samples.

3.2.2.3.7 Continuing calibration verification solution(s) must be analyzed, after every t samples and at the end of the run. The measured concentrations of the elements for which calibration was performed must be within 10% of their respective true values. If the continuing calibration verification solution doe not pass these criteria, reanalyze the CCV. If the CCV still fails criteria, th analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified prior to continuing sample analyse All samples run after the last acceptable CCV must be reanalyzed.

3.2.2.3.8 A continuing calibration blank is analyzed after every 10 samples and at the end of the run. Blanks are to be reported to the method detection limit. If t initial calibration blank result is greater than 3 times the standard deviation o the mean blank value, repeat the analysis two more times and average the results. If the average is less than 3 times the standard deviation of the background mean, then the data are acceptable and analyses may proceed. I the average is not within criteria, terminate the analysis, correct the problem recalibrate and reanalyze all samples analyzed since the last acceptable CCB.

3.2.2.4 Interelement correction factors are determined annually or after any major maintenance to the instrument by the following procedure:

3.2.2.4.1 Calibrate the instrument;

3.2.2.4.2 Aspirate individual solutions of each element at a concentration equal to its upper linear range and record the "apparent concentration" values produced at each channel for the remaining elements.

3.2.2.4.3 Divide the apparent concentration of analyte by the known concentration of the interferant. This factor is then programmed into each method and will automatically be applied during analysis.

3.2.2.5 The torch height must be optimized whenever the D2 mirror and/or torch are replaced, or the indicent power and/or nebulizer gas flow rate are changed. The torch height is optimized by the following procedure:

3.2.2.5.1 Aspirate a 1 ppm Cd solution and collect intensity data at the wavelength peak at 1 mm intervals from 15 to 25 mm above the top o the work coil.

3.2.2.5.2 Repeat the above process using the calibration blank.

3.2.2.5.3 Determine the position at which the ratio of peak intensity to background (blank) is maximum.

3.2.2.6 Troubleshooting:

3.2.2.6.1 If poor precision or an intensity drop is noted, check the D2 mirror, torch injector tip, introduction system for clogs and smooth drainage. Follow the cleaning procedure outlined above and replace the nebuliz mirror or torch if necessary.

3.2.2.6.2 If the torch will not light, check the reset buttons and circuit breakers gas pressure and level and for leaks.

3.2.2.6.3 A service contract is maintained for the instrument. If normal maintenance and troubleshooting procedures do not correct a problem the service technician should be called. In addition, an annual preventive maintenance visit should be scheduled with the service technician.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE

Sampling procedures are defined in the appropriate field SOPs. Dissolved metals should no be preserved until after sample filtration. Soil samples are collected in 1 pint wide-mouth mason jars. It is required that the samples be chilled to 4 deg. C (°C) immediately followin sampling. Water samples are collected in 1 L acid precleaned polyethelene plastic containe and preserved to pH <2.0 with nitric acid. Cooling of water samples is not required.

4.2 CONTAINERS

Sampling containers used are wide-mouth 500 mL amber jar for soils and 1 L nitric acid rinsed polyethelene cubitainers.

4.3 STORAGE CONDITIONS

Samples are stored at 4°C. in a walk-in refrigerator for soils. Water samples are stored at room temperature.

4.4 HOLDING TIMES

The holding time for digestion and analysis is 6 months from time of sampling.

4.5 SOLUTION VERIFICATION

Verification of the calibration standard stock solution is performed by analysis of a referenc solution which is analyzed with every run. The reference solution is a solution of known concentration prepared from stock standards that were purchased from a different manufacturer than those stock standards from which the calibration standards were prepared

Verification of the daily control spike stock solutions will be performed within one week prior to use for control spikes. Confirmation can occur by obtaining acceptable control spi recoveries (100 ± 10%) for high spike control spikes digested within one week of current spiking or direct analysis of a dilution of the stock solution within one week prior to spikin

5.0 DIGESTION AND ANALYSIS PROCEDURE

5.1 DIGESTION PROCEDURE FOR WATERS

Total recoverable metals: The entire sample is acidified, at the time of collection, with nitr acid. At the time of analysis, the sample is heated with nitric acid and substantially reduce in volume. The digestate is filtered, diluted to volume and is then ready for analysis.

Dissolved metals: The sample is filtered through a 0.45 μm filter and the filtrate acidified with nitric acid. Both filtration and acidification are performed at the time of collection. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as the standards.

5.1.1 Digestion Procedure for Water Samples (SW-846/3005):

5.1.1.1 Obtain and/or prepare the required quality control samples for digestion (see next section titled Water digestion quality control samples).

5.1.1.2 Using a graduated cylinder, transfer a 50 mL aliquot of well mixed sample t a beaker.

5.1.1.3 Add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl. The sample is covered with a ribbed watch glass and heated on a hot plate at 90 to 95°C until the volume has been reduced to 10 to 15 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

5.1.1.4 Remove the beaker and allow the sample to cool. Add 1.5 mL conc. HNO_3 to the digestate. Wash down the beaker walls with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the ICP nebulizer during analyses. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilut HNO_3 prior to use.

5.1.1.5 Adjust the final volume to 50 mL with Type II water. The digested samples should have an approximate acid concentration of 5% (v/v) HCl and 5% (v/v HNO_3.

5.1.1.6 Record the prep in the ESE prep logbook. Include the method number and any reagents used (with date prepared, lot numbers and expiration date). Place a copy of the logbook page in the box with the digestates.

5.1.1.7 Prepare labels for the sample bottles and sample box that will contain them.

5.1.1.8 Enter digestion date in the computer.

5.1.2 Water Digestion Quality Control Samples:

5.1.2.1 Preparation Blank - For each analytical batch of samples prepared, preparatio (method) blanks (Type II water plus reagents) are taken through the entire sample preparation and analytical processes to determine if the samples were contaminated during their preparation. The preparation blank for waters is th same sample as the unspiked control spike. Blanks are prepared at a frequency of 5% .

5.1.2.2 Low and Replicate High Control Spikes - Three Laboratory Control Samples (standard matrix spike) are included with each batch of samples. These samples are 50 mL aliquots of Type II water spiked with the correct volume of the USAEC ICP water spiking solution (see Table 7.1-1 for preparation). T correct volume is 0.5 mL for the low spike and 5.0 mL for each high spike. If the samples are to be analyzed for Tin and/or Molybdenum, 100 uL of the 1000 ppm Sn and/or Mo stock standard is also added to the two high spikes (target in the digestate will be 2.0 mg Sn and-or Mo/L). Laboratory control samples are used to determine accuracy and precision.

5.1.2.3 Matrix Spikes - Duplicate spiked environmental samples are prepared, at a frequency of 5%, with each batch of samples to be analyzed. Two 50 mL aliquots of a sample are each spiked with 5 mL of ICP Matrix Spiking Solution (see Table 7.2-1). If the samples are to be analyzed for Tin and/or Molybdenum, 100 uL of the 1000 ppm Tin and/or Molybdenum stock standa is also added to the spiked samples (target in the digestate will be 2.0 ug Sn and-or Mo/mL). Duplicate spikes are used to determine precision and matri effects. Note:a single spike only is required for TCLP samples.

Note: The actual number of Matrix spike QC required is rounded up to the nearest whole number, i.e., 5% = 1 QC for 1-20 samples; 2 QC for 21-40 samples, etc. The number of samples in this calculation should be installation (USAEC project) specific. Some installations define the samples requiring matrix spikes. These samples are usually tagged with orange labels. Since Matrix spike QC will be performed per batch, tagged QC spikes may be dropped when to many samples have been tagged by the field and not distributed by collection date properly.

5.3 ANALYSIS PROCEDURES FOR WATERS - SW-846/6010

5.3.1 Obtain work assignment from the group leader and get the required box of digestate lot folder, and method summary which contains a typical run sequence.

5.3.2 Begin the daily start-up procedures and daily optimization and tuning defined in Section 3.2 for daily calibration.

5.3.3 Profile and calibrate using the standards listed in Table 3.2-1.

5.3.4 Make sure the instrument is set up and analyze the standards samples and QC with a minimum of 2 replicates per sample, making dilutions for any elements that exceed the linear range. If the relative percent difference (RPD) between the replicate readings is greater than 20% for an element whose concentration is 10 times the instrument detection limit, repeat the analysis once. If the RPD is still greater than 20%, an interference should be suspected.

5.3.5 Reanalyze the standards used in the calibration. The concentration values must be within 5% of their respective true values or the analysis must be terminated, the problem corrected and the instrument recalibrated.

5.3.6 Flush the system with the calibration blank for at least one minute before the analys of each sample.

5.3.7 Initial calibration verification solution(s) (ICV-19 and ICV-7) must be analyzed afte calibration and before any samples are analyzed. All values must be within 10% of their respective true values or the analysis must be terminated, the problem correcte the instrument recalibrated, and the calibration reverified prior to sample analyses.

5.3.8 The interference check solutions (ICS-A and ICS-AB) are analyzed at the beginning and end of each sample analysis run. Results must fall within 20% of the true valu If not, terminate the analysis, correct the problem, recalibrate, reverify the calibration, and reanalyze the samples.

5.3.9 A method blank (or preparation blank) must be carried through all sample preparatio procedures at a frequency of 5%. The method blank is analyzed prior to the analys of samples. The method blank fails criteria if the results are greater than 2 times th method detection limit or the project-specific detection limit. If the method blank fails criteria, all samples prepared with the method blank must be redigested and the newly prepared samples analyzed or an appropriate explanation provided as to why the data should be acceptable. For water samples the method blank and the unspike control sample is the same sample.

5.3.10 The unspiked control sample and the three laboratory control samples (one low and replicate high standard matrix spikes). The measured concentrations of the element for which calibration was performed must be within the decision limits of their respective true values (see control charts). If the standard matrix spike(s) fail criter the analysis is terminated and the samples redigested and reanalyzed or an appropria explanation must be provided as to why the original samples should be acceptable.

5.3.11 Run samples, matrix spikes, serial dilution samples and analytical spikes to finish th ten spaces before CCV/CCB samples are required.

5.3.12 Continuing calibration verification solution(s) (CCV-1) must be analyzed, after eve ten samples and at the end of the run. The measured concentrations of the elements for which calibration was performed must be within 10% of their respective true values. If the continuing calibration verification solution does not pass these criteria reanalyze the CCV. If the CCV still fails criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified pri to continuing sample analyses. All samples run after the last acceptable CCV must be reanalyzed.

5.3.13 A continuing calibration blank (CCB) is analyzed after every 10 samples and at the end of the run. Blanks are to be reported to the method detection limit. If the initi calibration blank result is greater than 3 times the standard deviation of the mean blank value, repeat the analysis two more times and average the results. If the average is less than 3 times the standard deviation of the background mean, then the data are acceptable and analyses may proceed. If the average is not within criteria, terminate the analysis, correct the problem, recalibrate and reanalyze all samples analyzed since the last acceptable CCB.

5.3.14 A post-digestion spike (analytical spike) must be analyzed at a frequency of 5% Spik recoveries for all elements should fall within 75% to 125%, inclusive. If the spike i not recovered within the specified limits, a matrix effect should be suspected (5 mL sample to 5mL CCV solution).

5.3.15 The ICP serial dilution analysis (a 1+4 or 1:5 dilution of a prepared sample) must b analyzed with each batch of 20 or fewer samples of the same matrix type taken from the same project. If the analyte concentration in the sample is sufficiently high (minimally a factor of 10 above the instrument detection limit after the sample has been diluted), an analysis of the 1+4 dilution should agree within 10% of the measured concentration in the undiluted sample. If the results do not fall within thi criteria, a chemical or physical interference should be suspected.

5.3.16 The method summary contains an outline of a typical ICP run sequence. Acceptanc criteria is included for each step in the procedure section and in the run sequence. If an analysis fails criteria and reanalysis can not be performed, document the problem and consult your supervisor.

6.0 CALCULATIONS

The ICP is internally calibrated based on the daily calibration and the instrument provides extract concentration units in ug/mL. An ascii file of the instrument printout is read by an upload program in the CLASS™ (Chemical Laboratory Analysis Scheduling System) is ESE's computerized data management system and the ug/mL values are stored in the ESE data batch for each properly code sample and QC. Aqueous samples are converted to final concentration from ug/mL to ug/L. If a dilution was required, the concentration in the diluted sample and the dilution factor are reported i the data batch.

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SPIKES FOR WATERS

The USAEC ICAP water spike solution is prepared (see Table 7.1-1) by adding the indicate volumes of stock solutions to a 1000 mL volumetric flask containing distilled water and 200 mL of concentrated HCl and then diluting to volume with distilled water. A low level and replicate high level daily control spikes are prepared by adding 0.5 mL for the low spike an 5.0 mL for each high spike of the USAEC ICAP water spiking solution to 50 mL of distille water. The control spikes are digested and analyzed according to Sections 5.1 and 5.3, respectively.

7.2 MATRIX SPIKE SOLUTION FOR WATERS

An aliquot of each stock standard (as outlined in Table 7.2-1) is added to a 1000 mL volumetric flask containing type II water and 200 mL concentrated HCl and then diluted to volume with type II water. This solution is prepared fresh every 33 days. The manufacturer, lot number and expiration date for each stock solution are entered in the standard prep logbook. Typically 5.0 mL of spiking solution is added to 50 mL of aqueous solutions and 10.0 mL is added to soil preps which have a final volume of 100 mL. The target concentrations in the digestate are listed in the above table.

Table 7.1-1. Preparation of USAEC ICP Water Spike Solution and Target Control Spike Concentrations.

Element	Stock Conc. (mg/L)	Volume Added (mL)	ICAP Spike Solution Conc. (mg/L)	Low Spike (SP1) Target (ug/L)	High Spike (SP2, SP3) Target (ug/L)
Aluminum	10,000	0.8	8	80	800
Antimony	1,000	10	10	100	1000
Arsenic	1,000	20	20	200	2000
Barium	1,000	5	5	50	500
Beryllium	1,000	1	1	10	100
Boron	1,000	10	10	100	1000
Cadmium	1,000	1	1	10	100
Calcium	10,000	2	20	200	2000
Chromium	1,000	2	2	20	200
Cobalt	1,000	4	4	40	400
Copper	1,000	1	1	10	100
Iron	10,000	0.9	90	90	900
Lead	1,000	10	10	100	1000
Magnesium	10,000	1	10	100	1000
Manganese	1,000	1	1	10	100
Molybdenum	1,000	2	2	20	200
Nickel	1,000	3	3	30	300
Potassium	10,000	11	110	1100	11,000
Selenium	1,000	20	20	200	2000
Silver	1,000	1	1	10	100
Sodium	10,000	2	20	200	2000
Thallium	1,000	20	20	200	2000
Tin	1,000	10	10	100	1000
Vanadium	1,000	2	2	20	200
Zinc	1,000	10	10	100	1000

Table 7.2-1. Preparation of Water ICP Matrix Spike Solution.

Element	Stock Conc. (mg/L)	Volume Added (mL)	Final conc. (mg/L)	Target in Digestate (mg/L)
Aluminum	10,000	2.0	20.0	2.0
Antimony	1,000	5.0	5.0	0.5
Arsenic	1,000	20.0	20.0	2.0
Barium	1,000	20.0	20.0	2.0
Beryllium	1,000	0.5	0.5	0.05
Cadmium	1,000	0.5	0.5	0.05
Calcium	10,000	10.0	100.0	10.0
Chromium	1,000	2.0	2.0	0.2
Cobalt	1,000	5.0	5.0	0.5
Copper	1,000	2.5	2.5	0.25
Iron	10,000	1.0	10.0	1.0
Lead	1,000	5.0	5.0	0.5
Magnesium	10,000	10.0	100.0	10.0
Manganese	1,000	5.0	5.0	0.5
Nickel	1,000	5.0	5.0	0.5
Potassium	10,000	10.0	100.0	10.0
Selenium	1,000	20.0	20.0	2.0
Silver	1,000	0.5	0.5	0.05
Sodium	10,000	10.0	100.0	10.0
Thallium	1,000	20.0	20.0	2.0
Vanadium	1,000	5.0	5.0	0.5
Zinc	1,000	5.0	5.0	0.5

7.3 CONTROL CHARTS

The control charts are designed to monitor laboratory control situations which are generally tighter than method performance acceptance criteria. Therefore the burden is on the analys and the laboratory to understand their systems and required action limits in order to observ trends with assistance from the control charts and provide sufficient explanations and corrective actions when trends or outside control limit conditions occur in order for an analytical lot to be considered acceptable. Acceptance is usually determined from decision limits which are generally outside control chart limits because control chart limits (especial for replicate high spikes) ignore day to day variability. Therefore control limits are tight compared to typical standard deviation charts when within day variability of replicates is tighter than normal day to day variability. This type of chart is useful because it forces the question to be asked: "Can daily calibration be controlled more closely?". If the answer is no then alternative decision limits become more important and trends need to be reviewed i relation to the alternate limits. Control charts and corrective action explanations are reviewed summarized and provided weekly by Project Management and QA Staff to USAE for acceptance of a Lot.

The USAEC control chart program requires input for analysis date, lot name, target and found results for each control spike.

8.0 REFERENCES

U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects, May 1993.

Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standard General Industry" (29 CFR 1910), (Revised, January 1976).

Federal Register, Vol. 44, No. 233, 1979. Inductively Coupled Plasma (ICP) Optical Emission Spectroscopic Method for Trace Element Analysis of Water and Wastes.

EPA Method 3005 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

EPA Method 3050 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

EPA Method 6010 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

Federal Register - Volume 4 Number 136, Appendix B.

9.0 APPENDICES

9.1 ORGANIZATION FOR LOT FOLDER
- see ATTACHMENT 1

9.2 METHOD SUMMARIES FOR LOT FOLDER
- see ATTACHMENT 2

9.3 INITIAL MDL RESULTS TO SUPPORT REPORTING LIMITS
- see ATTACHMENT 3

ATTACHMENT 1
ORGANIZATION FOR LOT FOLDER

TABLE OF CONTENTS — METALS

A. TRANSMITTAL DOCUMENTS
(to be supplied by Information Services)

_____1. Army Data Review Form
_____2. IRDMS Transfer File
_____3. Results of IRDMS Record and Group Check

B. ANALYST DOCUMENTS

_____1. Method Summary (supplied by Information Services)
_____2. ESE Data Batch Report, with:
a. Analyst Signature
b. Computer Checklist
c. Manual Checklist
d. Example Calculation
_____3. Completed Control Chart and Comment/Corrective Action Form
_____4. Copies of Instrument Logbook Pages (with analytical conditions)
_____5. Raw Data, with:
a. Responses (emission/area counts, peak heights, etc.)
b. Calibration Curve
c. Changes made properly and initialed
_____6. Copies of Sample Extract/Prep Logbook Pages
_____7. Chain-of-Custody and Possession Records
a. Field Chain-of-Custody Sheets (supplied by Info. Services)
b. Laboratory Subsample Chain-of-Custody

C. APPENDIX
_____1. Preliminary Data, Unused Data (if applicable)
_____2. Laboratory Coordinator and QA Review Files
_____3. Validation File in USATHAMA Format

Note: each of the above documents should be numbered and placed in the lot folder in the order indicated.

ATTACHMENT 2
METHOD SUMMARIES FOR LOT FOLDERS

December 8, 1993

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.:	Aqueous Samples by ICAP	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC Soil Spike Solutions - see table 7.1-1 and 7.2-1 for preparation.

2. Prepare quality control samples:
   a. Method blank (MB) - reagents only.
   b. Low Spike (SP1) - add 0.5 mL of spike solution to 50 mL detionized water.
   c. High Spike (SP2, SP3) - add 5 mL of spike solution to 50 mL deionized water. If the samples are to be analyzed for Tin and/or Molybdenum, 100 uL of the 1000 ppm Sn and/or Mo stock standard is also added to the two high spikes (target in the digestate will be 2.0 mg Sn and-or Mo/L).
   d. Matrix Spikes (SPM1, SPM2) - Two 50 mL aliquots of a sample are each spiked with 5 mL of ICP Matrix Spiking Solution (see Table 7.2-1). If the samples are to be analyzed for Tin and/or Molybdenum, 100 uL of the 1000 ppm Tin and/or Molybdenum stock standard is also added to the spiked samples (target in the digestate will be 1.0 ug Sn and-or Mo/mL). Duplicate spikes are used to determine precision and matrix effects.

DIGESTION PROCEDURE:

1. Using a graduated cylinder, transfer a 50 mL aliquot of well mixed sample to a beaker.

2. Add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl. The sample is covered with a ribbed watch glass and heated on a hot plate at 90 to 95°C until the volume has been reduced to 10 to 15 mL. CAUTION: Do not boil. Antimony is easily lost by volatilization.

3. Remove the beaker and allow the sample to cool. Add 1.5 mL conc. HNO_3 to the digestate. Wash down the beaker walls with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the ICP nebulizer during analyses. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute HNO_3 prior to use.

4. Adjust the final volume to 50 mL with Type II water. The digested samples should have an approximate acid concentration of 5% (v/v) HCl and 5% (v/v) HNO_3.

5. Record the prep in the ESE prep logbook. Include the method number and any reagents used (with date prepared, lot numbers and expiration date). Place a copy of the logbook page in the box with the digestates.

6. Prepare labels for the sample bottles and sample box that will contain them.

7. Enter digestion date in the computer.

Number	TITLE	QC REFERENCE
USAEC No.:	Aqueous Samples by ICAP	USAEC/SW846

INSTRUMENT ANALYSIS:

1.. Optimize, profile and calibrate using the standards listed in Table 3.2-1.
2. Analyze the standards samples and QC with a minimum of 2 replicates per sample, making dilutions for any elements that exceed the linear range. If the relative percent difference (RPD) between the replicate readings is greater than 20% for an element whose concentration is 10 times the instrument detection limit, repeat the analysis once. If the RPD is still greater than 20%, an interference should be suspected.
3. Reanalyze the standards used in the calibration. Values must be within 5% of their respective true values or the analysis must be terminated, the problem corrected and the instrument recalibrated.
4. Flush the system with the blank for at least one minute before the analysis of each sample.
5. Analyze the ICVs. All values must be within 10% of their respective true values or the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified prior to sample analyses.
6. ICS-A and ICS-AB are analyzed at the beginning and end of each sample analysis run. Results must fall within 20% of the true value. If not, terminate the analysis, correct the problem, recalibrate, reverify the calibration, and reanalyze the samples.
7. A reagent blank is analyzed prior to the analysis of samples. If the reagent blank is greater than 2 times the method detection limit or the project-specific detection limit. All samples prepared with the reagent blank must be redigested and the newly prepared samples analyzed or an appropriate explanation provided as to why the data should be acceptable.
8. The method blank and the three laboratory control samples (one low and replicate high standard matrix spikes). The measured concentrations of the elements for which calibration was performed must be within control chart limits. If the standard matrix spike(s) fail criteria, the analysis is terminated and the samples redigested and reanalyzed or an appropriate explanation must be provided as to why the original samples should be acceptable.
9.. Analyze samples, matrix spikes.
10.. A CCV must be analyzed, after every ten samples and at the end of the run. If the CCV is not within 10% of the respective true values, reanalyze the CCV once. If the CCV still fails criteria, the instrument is recalibrated and all samples run after the last acceptable CCV reanalyzed.
11. A CCB is analyzed after every 10 samples and at the end of the run. If the CCB is greater than 3 times the standard deviation of the mean blank value, repeat the analysis two more times and average the results. If the average is less than 3 times the standard deviation of the background mean, then the data are acceptable and analyses may proceed. If the average is not within criteria, recalibrate and reanalyze all samples analyzed since the last acceptable CCB.
12. A post-digestion spike (analytical spike) must be analyzed at a frequency of 5% Spike recoveries for all elements should fall within 75% to 125%, inclusive. If the spike is not recovered within the specified limits, a matrix effect should be suspected (5 mL sample to 5mL CCV solution).
13. Do a serial dilution analysis (a 1+4 or 1:5 dilution of a prepared sample) with each batch of 20 samples. If the concentration is sufficiently high (minimally a factor of 10 above the instrument detection limit after the sample has been diluted), an analysis of the 1+4 dilution should agree within 10% of the measured concentration in the undiluted sample. If the results do not fall within this criteria, a chemical or physical interference should be suspected.

Number	TITLE	QC REFERENCE
USAEC No.:	Aqueous Samples by ICAP	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS data batch.
2. If the method blank has a response greater than the instrument detection limit, blank correction should be applied to the daily control spikes only. If the MB (or any sample with a matrix spike) has a negative response or is less than the instrument detection limit, enter the response as 0 Final.
3. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.
4. Generate spike recovery/control chart data for Information Services.

Typical ICP Run Sequence for USACE ICP Waters Run -SW846

Calibration blank	
Standard 1 through Standard 5	
Rerun Standard 2 through 5	$\pm$ 5%
Initial Calibration Verification (ICV-19)	$\pm$ 10%
Initial Calibration Verification (ICV-7)	$\pm$ 10%
Interference Check Sample (ICS-A)	$\pm$ 20%
Interference Check Sample (ICS-AB)	$\pm$ 20%
Preparation/Method Blank (MB)	
Low Spike - (SP1)	see control charts*
High Spike - (SP2)	see control charts*
High Spike - (SP3)	see control charts*
Sample #1	
Sample #1 matrix spike (SPM1)	
Sample #1 matrix spike dup (SMP2)	
Sample #2	
Sample #2 serial dilution (1+4)	$\pm$ 10%
Sample #3	
Continuing Calibration Verification, CCV	$\pm$ 10%
Continuing Calibration Blank, CCB	
Sample #3 analytical spike	$\pm$ 25%
Sample #4 through Sample #12	
Continuing Calibration Verification, CCV	$\pm$ 10%
Continuing Calibration Blank, CCB	
Sample #13 through Sample #22	
Continuing Calibration Verification, CCV	$\pm$ 10%
Continuing Calibration Blank, CCB	
Method Blank (MB-2)	
Sample #23	
Sample #23 matrix spike (SPM1)	
Sample #23 matrix spike dup (SMP2)	
Sample #24	
Sample #24 serial dilution (1+4)	$\pm$ 10%
Sample #25	
Sample #26	
Sample #26 analytical spike	$\pm$ 25%
Sample #27	
CCV	$\pm$ 10%
CCB	Sample #35
Sample #28 through 35	
ICS-A	$\pm$ 20%
ICS-AB	$\pm$ 20%
CCV	$\pm$ 10%
CCB	

*Charts are reviewed for trends action limits are $\pm$ 25% for low spike control elements and $\pm$ 15% for high spike control elements.

ATTACHMENT 3
MDL RESULTS TO SUPPORT REPORTING LIMITS

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: DETERMINATION OF METALS IN SOIL BY INDUCTIVELY COUPLED ARGON PLASMA SPECTROSCOPY (SW-846/3050/6010) USAEC METHOD - ICP1 - SOIL

TABLE OF CONTENTS

**TITLE: DETERMINATION OF METALS IN SOIL SAMPLES BY INDUCTIVELY COUPLED ARGON PLASMA SPECTROSCOPY (SW-846/3005/6010)
USAEC METHOD - ICP1 - SOIL**

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This ESE standard operating procedure follows EPA SW-846 protocols with additional quality control requirements applicable for the Class 1 analysis under the USAEC guidelines for implementation of ER 1110-1-263 of the following elements in environmental soil and sediment samples:

Element	Chemical Symbol
Silver	Ag
Aluminum	Al
Arsenic	As
Boron	B
Barium	Ba
Beryllium	Be
Calcium	Ca
Cadmium	Cd
Cobalt	Co
Chromium	Cr
Copper	Cu
Iron	Fe
Potassium	K
Magnesium	Mg
Manganese	Mn
Molybdenum	Mo
Sodium	Na
Nickel	Ni
Lead	Pb
Antimony	Sb
Selenium	Se
Tin	Sn
Thallium	Tl
Vanadium	V
Zinc	Zn

1.2 GENERAL METHOD

This method employs an acid digestion (using Nitric - HNO_3 and Hydrochloric - HCl acid) of a soil (SW-846 Method 3050) followed by analysis of the digestate by simultaneous inductively coupled argon plasma (ICP) spectroscopy (SW-846 Method 6010). This method is equivalent to the SW-846 methods except that the final acid concentration for sample digestates, standards and quality control is 5% (v/v) HNO_3 and 5% (v/v) HCl. These modifications are minor to the spirit of the SW-846 methods because digestates have been adjusted after digestion and prior to returning to final digestate volume and matrix matching of standards and samples is considered acceptable laboratory practice for avoiding matrix biases.

Additional quality control samples required by USAEC have been added to the SW-846 requirements: 1) primarily daily control spikes - one spike at two times the reporting limit and two spikes at twenty times the reporting limit; and 2) initial calibration requirements must cover the range of the reporting limit and the upper range where no dilution is required. The following analytes are typically analyzed by this method for the following analytical requests:

EPA TAL List	EPA PP List	TCLP List
Al	Be	As
Ba	Cd	Se
Be	Cr	Ag
Ca	Cu	Pb
Cd	Ni	Cr
Co	Zn	Ba
Cr		Cd
Cu	Ag*	
Fe	Tl*	
K	Pb*	
Mg		
Mn		
Na		
Ni		
V		
Zn		
Ag*		
Pb*		
Tl*		
Sb*		

* These analytes are analyzed by ICP unless GFAA methods are specifically required.

1.3 REPORTING LIMITS AND INITIAL CALIBRATION RANGES - SOILS

MDL studies are performed quarterly to confirm the validity of the chosen reporting limit following the procedure outlined in 40CFR Volume 4 No. 136, Appendix B. Initial calibration must cover the entire range from the reporting limit to the upper range beyond which dilutions are required. The method detection limits, and upper and lower initial calibration standard range for ICAP Metals in Soil - Method 3050/6010 are as follows:

Parameter	Reporting Limit (ug/g)	Lower Standard Range (ug/g)[2]	Upper Standard Range (ug/g)[2]
Aluminum[1]	10.0	10.0	100,000
Antimony	5.0	5.0	10,000
Arsenic	10.0	10.0	10,000
Barium[1]	5.0	5.0	10,000
Beryllium	0.5	0.5	10,000
Boron	5.0	5.0	10,000
Cadmium	0.5	0.5	10,000
Calcium[1]	20.0	20.0	100,000
Chromium	1.0	1.0	10,000
Cobalt	2.0	2.0	10,000
Copper	0.5	0.5	10,000
Iron[1]	10.0	10.0	100,000
Lead	5.0	5.0	10,000
Magnesium[1]	10.0	10.0	100,000
Manganese[1]	0.5	0.5	10,000
Molybdenum	1.0	1.0	10,000
Nickel	2.0	2.0	10,000
Potassium[1]	60.0	60.0	100,000
Selenium	10.0	10.0	10,000
Silver	0.5	0.5	10,000
Sodium[1]	20.0	20.0	50,000
Thallium	10.0	10.0	10,000
Tin	5.0	5.0	10,000
Vanadium	1.0	1.0	10,000
Zinc	5.0	5.0	10,000

[1] The parameter may be analyzed by the referenced method, but it is not a control analyte for the method.
[2] Based on 1 g of soil sample and 100 mL end volume.

1.4 INTERFERENCES

Broadly defined, an interference is any unwanted radiation that reaches the photomultiplier tubes. It can arise from background continuum or as true spectral interferences. Sources of background continuum are black-body radiation, bremsstrahlung radiation, and recombination phenomena. These are compensated for by spectrum shifting," i.e., measuring emission intensity on both sides of each analytical line. The average radiation detected "off-center" is subtracted from the intensity measurement taken at the analytical line. Spectral interferences occur when the wavelength separation of the emission lines is less than the spectral bandpass of the detector. By determining the ratio of interfering element to affected element, the computer is programmed to discount the unwanted radiation. These interelement corrections are usually small for water samples. Iron, for example, will give rise to a false signal for cadmium, but the ratio is less than 1:1,000. Magnesium interferes with chromium, but again the effect is quite small. No major interferences were encountered during the documentation of this method. Interelemental correction factors were applied when using the simultaneous instrument.

1.5 ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 35 samples in an 8-hour day. Approximately 35 samples can be digested in an 8-hour day.

1.6 SAFETY INFORMATION

This method involves digestion of aqueous samples with a mixture of nitric acid and hydrochloric acid. Both of these reagents are corrosive and adequate dermal and eye protection are required. Sample digestions should be carried out in a hood with adequate ventilation.

2.0 APPARATUS AND CHEMICALS

2.1 GLASSWARE/HARDWARE

2.1.1 Analytical balance - capable of accurately weighing 0.1 mg;

2.1.2 Griffin beakers or erlenmeyer flasks (150 mL);

2.1.3 Watch glasses or erlenmeyer covers;

2.1.4 Filter funnels and Whatman No. 41 filter paper, or equivalent;

2.1.5 Graduated cylinders (50 mL and 100 mL);

2.1.6 Electric hotplate adjustable and capable of maintaining 90-95°C.

2.1.7 Class A volumetric pipet (10, 5-mL);

2.1.8 Adjustable Eppendorf or equivalent micropipettor (100 and 1000 uL);

2.1.9 Disposable beakers (10-mL).

2.1.10 Class A volumetric flasks (1000, 500, 200, 100, and 10 mL).

2.1.11 Class A volumetric pipettes.

2.1.12 Automatic pipetter, Repipet^R or equivalent.

2.2 INSTRUMENTATION

2.2.1 Jarrell-Ash 1100(J.A. 1100) Series Mark III Plasma AtomComp Spectrometer or Jarrell-Ash 61E(J.A.61E) equipped with spectrum shifter for background correction. The approximate instrument settings are as follows:

a) Incident RF power - 1.05 kilowatts (kw),

b) Reflected RF power - minimized (<3 kW),

c) Observation height - 20 mm above coil,

d) Sample argon flow rate - 0.5 L/min, and

e) Coolant argon flow rate - 20 L/min.

NOTE: Daily instrument settings may vary due to environmental conditions and the nature of the samples being analyzed. Check solutions and daily control spikes will verify the instrument optimization.

2.3 CHEMICALS AND REAGENTS

2.3.1 Ultra pure concentrated nitric acid and hydrochloric acid.

2.3.2 Stock solutions are purchased for preparing calibration, spiking, reference, and interference check solutions. Solutions must be traceable to NIST standard reference material (vendors include could be Inorganic Ventures, Inc.; High Purity, Inc.; SPEX Industries, Inc. and Perkin Elmer).

2.3.3 The water used for dilution of standards, certification spiking, sample preparation and analysis is ASTM Type I grade (American Society for Testing Materials, Philadelphia, PA.).

2.3.4 Hydrogen peroxide (H2O2); 30%, trace metals grade, Fisher or equivalent distributer.

2.3.5 USAEC Standard Soil.

2.4 ANALYTES

The Chemical Abstract Service (CAS) registry numbers and instrumental wavelengths are as follows and are element specific:

Analyte	CAS Registry Number	Operating Wavelength (nm) J.A. 1100	Operating Wavelength (nm) J.A. 61E
Ag	7440-22-4	328.0	328.0
Al	7429-90-5	308.2	308.2
As	7440-38-2	193.6	193.6
B	7440-42-8	249.7	249.7
Ba	7440-39-3	493.4	493.4
Be	7740-41-77	234.8	313.0
Ca	7440-70-2	317.9	317.9
Cd	7740-43-9	228.8	228.8
Co	7440-48-4	228.6	228.6
Cr	7440-47-3	267.7	267.7
Cu	7440-50-8	324.7	324.7
Fe	7339-89-6	259.9	259.9
K	7440-09-7	766.5	766.5
Mg	7439-95-4	277.0	279.0
Mn	7439-96-5	257.6	257.6
Mo	7439-98-7	202.0	202.0
Na	7440-23-5	589.0	589.0
Ni	7740-02-0	231.6	231.6
Pb	7439-92-1	220.3	220.3
Sb	7740-36-0	217.5	206.8
Se	7782-49-2	196.0	196.0
Tl	7740-28-0	190.8	190.8
V	7440-62-2	292.4	292.4
Zn	7740-66-6	213.8	213.8

3.0 CALIBRATION

3.1 INITIAL CALIBRATION

An initial calibration will be performed after any of the following:

* Major instrument maintenance;
* Instrument modification;
* Replacement of the torch;
* Replacement of the mirror, or
* The daily calibration slope is not within the acceptance criteria of $\pm$ 10 % of the last initial calibration slope.

When initial calibration is required, a minimum of five standards for each element will be analyzed. The standards will consist of a blank, a standard at the reporting limit, two intermediate standards (the daily calibration level and a 1:1 dilution of the daily calibration level) and a standard at the upper linear range. A standard curve will be constructed for each element by plotting the measured response versus the known concentration. The best-fit linear regression line obtained for each metal must have a correlation coefficient (CC) of 0.995 or higher. If the CC is less than 0.995 for any element, the standards for that element must be prepared again and/or a lower upper range standard must be used.

Table 3.1-1 defines and summarizes the preparation of the required initial calibration standards. Table 3.1-1 alsopresents the water reporting limits for comparison to the MDL-1 solution. Dilutions of the MDL-1 solution are prepared to meet MDLs for all elements for initial calibration. The WMDL-1 solution is used for MDL studies and is prepared with 20 % HCL to lengthen the life of the solution (especially for Ag). All solutions injected have an acid concentration of 5% (v/v) HCl and 5% (v/v) HNO3.

Table III-1. Preparation Scheme for Initial Calibration Standards.

	STOCK CONC. mg/L	UPPER RANGE STANDARD ID	MLS STOCK USED (10 ml FINAL VOLUME) mL	FINAL CONC. UPPER RANGE STD. mg/L	MID RANGE STD ID	MLS STOCK USED (1 L FINAL VOLUME) mL	FINAL CONC. MID RANGE STD. mg/L	1:1 MID RANGE STANDARD ID	ML MRS USED (50 mL FINAL VOLUME) mL	FINAL CONC 1:1 MID RANGE STD. mg/L	WORKING MDL STOCK ID	ML STOCK USED (100 mL FINAL VOLUME mL	CONC WORKING MDL STOCK mg/L	MDL STD ID	CONC MDL STD 1:100 OF WMDL-1 ug/L	WATER MDL ** ug/L
As	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	1.0	10	MDL-1	100	100
B	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.5	5.0	MDL-1	50	50
Ba	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.05	0.5	MDL-1	5.0	25
Be	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.05	0.5	MDL-1	5.0	5.0
Cd	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.1	1.0	MDL-1	10	5.0
Co	1000	URS-1	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.3	3.0	MDL-1	30	20
Cr	1000	URS-2	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.2	2.0	MDL-1	20	10
Cu	1000	URS-2	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.1	1.0	MDL-1	10	5.0
Mn	1000	URS-2	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.05	0.5	MDL-1	5.0	5.0
Ni	1000	URS-2	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.5	5.0	MDL-1	50	15
Pb	1000	URS-2	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	1.0	10	MDL-1	100	50
Sb	1000	URS-3	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	1.0	10	MDL-1	100	100
Se	1000	URS-3	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	1.5	15	MDL-1	150	100
Tl	1000	URS-3	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	2.0	20	MDL-1	200	100
V	1000	URS-3	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.15	1.5	MDL-1	15	10
Zn	1000	URS-3	1.0	100	MRS-1	1.0	1.0	MRS.5-1	25	0.5	WMDL-1	0.1	1.0	MDL-1	10	20
Al	10000	URS-4	1.0	1000	MRS-2	1.0	10.0	MRS.5-2	25	5.0	WMDL-1	0.1	10	MDL-1	100	40
Ca	10000	URS-4	1.0	1000	MRS-2	1.0	10.0	MRS.5-2	25	5.0	WMDL-1	0.1	10	MDL-1	100	100
Fe	10000	URS-4	1.0	1000	MRS-2	1.0	10.0	MRS.5-2	25	5.0	WMDL-1	0.05	5.0	MDL-1	50	45
K	10000	URS-4	1.0	1000	MRS-2	10.0	100	MRS.5-2	25	50	WMDL-1	1.5	150	MDL-1	1500	550
Mg	10000	URS-4	1.0	1000	MRS-2	1.0	10.0	MRS.5-2	25	5.0	WMDL-1	0.1	10	MDL-1	100	50
Na	10000	URS-5	1.0	1000	MRS-2	1.0	10.0	MRS.5-2	25	5.0	WMDL-1	0.2	20	MDL-1	200	100
Ag	1000	URS-5	1.0	100	MRS-3	1.0	1.0	MRS.5-3	25	0.5	WMDL-1	0.15	1.5	MDL-1	15	5.0
Mo	1000	URS-5	1.0	100	MRS-3	1.0	1.0	MRS.5-3	25	0.5	WMDL-1	0.15	1.5	MDL-1	15	10
Sn	1000	URS-5	1.0	100	MRS-3	1.0	1.0	MRS.5-3	25	0.5	WMDL-1	1.0	10	MDL-1	100	50

NOTES: All solutions for instrument are made up for 5% (v/v) HNO_3 5% (v/v) HCl. The WMDL-1 Solution is made up for 20 % (v/v) HCL. Dilutions of MDL-1 are prepared to meet all reporting limits.

** The water MDL column is provided for reference to show which compounds will require a dilution of the MDL-1 standard in order to ensure that the initial calibration curve includes a standard at or below the reporting limit. The soil MDL are always equal to or higer than the water MDLs.

The solutions listed in Table 3.1-1 are named and defined as follows
URS-x = Upper range standard with x representing a solution containing certain elements.
MRS-x = Mid range standard with x representing a solution containing certain elements.
MRS.5-x = A 1:1 dilution of the MRS with x representing a solution containing certain elements.
WMDL-1 = Working method detection limit standard stock.
MDL-1 = Method detection limit standard.

3.2 DAILY CALIBRATION

3.2.1 Preparation of Daily Calibration Solutions:
All standards and check solution preps are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date. Table 3.2-1 is presented as a summary and guide for preparation as discussed below. All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3 and 5% (v/v) HCl. In addition, different stock solutions should be used for preparation of the calibration standards, CCV, ICVs and the digestion spike solution. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst.
Mixed calibration standards are made by pipetting the appropriate (see Table 3.2-1) volume of each stock solution into a 1000 mL volumetric flask containing approximately 500 mL of Type II water, 50 mL of concentrated HNO_3 and 50 mL of concentrated HCl. The final volume is adjusted to 1000 mL with Type II water. Standard 1 (STD-1) is a calibration blank containing 5% (v/v) HNO_3 and 5% (v/v) HCl. The other solutions are named STD-2 through STD-5. These solutions expire in 33 days.
The continuing calibration verification solution (CCV-1) is prepared by adding the appropriate volume (see also Table 3.2-1) of stock standards to a 1000 mL volumetric flask containing 500 mL Type II water, 50 mL conc. HNO_3 and 50 mL conc. HCl. The final volume is adjusted to 1000 mL with deionized water. The CCV expires in 33 days.

Two multi-element initial calibration verification solution(s) (ICV) are prepared according to the manufacturer's instructions (see also Table 3.2-1). For SPEX reference solutions, 1.0 mL of the stock solution is added to a 100 mL volumetric flask containing 50 mL Type II water, 5 mL conc. HNO_3 and 5 mL conc. HCL. The final volumes are adjusted to 100 mL with Type II water. If an independent reference is not available, the ICV may be prepared from different stock solutions (manufacturer or lot number) than those used to prepare the calibration standards. The elemental concentrations of the ICV are prepared so that they are within the calibration range of the instrument but at concentrations other than those used for

instrument calibration. Elemental concentrations for the SPEX solutions are listed in Table 3.2-1. The prepared ICV solutions (ICV-7 and ICV-19) expire in 33 days.

Two multi-element interference check solutions (ICS) are prepared (see also Table 3.2-1) by adding the appropriate volume of stock PE-PURE multi-element CLP solutions to 100 mL volumetric flasks containing approximately 50 mL of Type II water, 5 mL of concentrated HNO_3, and 5 mL of concentrated HCl. ICS-A is prepared with 10 mL of solution A. ICS-B is prepared with 10 mL of solution A and 1 mL of solution B. Final volumes are adjusted to 100 mL with Type II water. The elemental concentrations of each solution are listed in Table 3.2-1. These solutions (ICS-A and ICS-AB) expire in 33 days.

The initial calibration blank (ICB) and continuing calibration blanks (CCB) are acidified deionized water (5% HNO_3 plus 5% HCl). This solution expires in 33 days.

Table 3.2-1. Preparation of Daily Calibration Standards and Check Solutions

ANALYTE		CALIBRATION STANDARDS		CONT. CALIB. VERIFICATION		INITIAL CALIB. VERIFICATION		INTERFERENCE CHECK SOLUTION					
CONC.	STOCK CONC.	STANDARD ID	VOLUME OF STOCK USED	STANDARD CONC.	CCV ID	VOLUME OF STOCK USED	CCV CONC.	ICV ID	STOCK CONC.	ICV CONC.	ICS	STOCKICS ID	CONC.
	(mg/L)		(mL)	(mg/L)		(mL)	(mg/L)		(mg/L)	(mg/L)		(mg/L)	(mg/L)
As	1,000	STD-2	1.0	1.0	CCV-1	0.7	0.7	ICV-19	100	1.0	--	--	--
Ba	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-7	100	1.0	ICS-AB	50	0.5
Be	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Cd	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	100	1.0
Co	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Cr	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Cu	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Mn	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Ni	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	100	1.0
Pb	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	100	1.0
Sb	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	--	--	--
Se	1,000	STD-2	1.0	1.0	CCV-1	0.7	0.7	ICV-19	100	1.0	--	--	--
Tl	1,000	STD-2	1.0	1.0	CCV-1	0.7	0.7	ICV-19	100	1.0	--	--	--
V	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	50	0.5
Zn	1,000	STD-2	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	ICS-AB	100	1.0
Al	10,000	STD-3	1.0	10.0	CCV-1	0.5	5.0	ICV-7	100	1.0	ICS-A	5000	500
Ca	10,000	STD-3	1.0	10.0	CCV-1	0.5	5.0	ICV-19	100	1.0	ICS-A	5000	500
Fe	10,000	STD-3	1.0	10.0	CCV-1	0.5	5.0	ICV-19	100	1.0	ICS-A	2000	200
K	10,000	STD-3	10.0	100.0	CCV-1	0.5	5.0	ICV-7	1000	10.0	--	--	--
Mg	10,000	STD-3	1.0	.10.0	CCV-1	0.5	5.0	ICV-19	100	1.0	ICS-A	5000	500
Na	10,000	STD-3	1.0	10.0	CCV-1	0.5	5.0	ICV-7	100	1.0	--	--	--
Ag	1,000	STD-4	1.0	1.0	CCV-1	0.5	0.5	ICV-7	100	1.0	ICS-AB	100	1.0
Mo	1,000	STD-5	1.0	1.0	CCV-1	0.5	0.5	ICV-19	100	1.0	--	--	--

Notes: STD-1 is the Calibration Blank. All solutions are made to a final acid concentration of 5% (v/v) HCl and 5% (v/v) HNO3.
STD and CCV solutions are made to final volumes of 1000 mL; ICV and ICS are made to a final volume of 100 mL.

3.2.2 Analysis of Calibration Standards and QC for Daily Calibration:

3.2.2.1 Instrument Daily start-up procedures:

3.2.2.1.1 Check the Argon tank level. The regulator should read approximately 80 psi. Turn on the water recirculator, computer, monitor, printer buffer box and printer. Install new peristaltic pump tubing daily and engage.

3.2.2.1.2 Open the coolant and sample valves on the front of the instrument. Aspirate deionized water for approximately 3 minutes watching for even flow through the tubing. Check capillary tubing for kinks or dust balls, replace or remove as necessary. Check the nebulizer for a fine even cloud. If clogged, remove the capillary tubing and spray canned air through the nebulizer. The nebulizer flow should be approximately 0.3 LPM.

3.2.2.1.3 Inspect the torch injector tip for fire polish or salt deposits. If necessary; remove and dip (not soak) the injector tip in 1+1 HF for 2-3 minutes. Rinse with water and reinstall. Replace the torch if it is chipped or uneven at the orifice. Note: if the torch is replaced, the torch height must be optimized.

3.2.2.1.4 Inspect the D2 mirror with a flashlight for dust or film. Dust may be blown off with canned air. If the mirror has a film, remove it being careful not to touch the face of the mirror. Clean by rinsing with isopropyl alcohol and then bottled distilled water. Dry completely with canned air and reinstall the mirror. Replace the mirror if it cannot be properly cleaned. Note: if the mirror is replaced, the torch height must be optimized.

3.2.2.1.5 Check the drain bucket and, if necessary, pour out some of the contents, but do not empty below the line indicated on the bucket. Also empty the dehumidifier bucket.

3.2.2.1.6 After aspirating deionized water for a few minutes, close the sample valve and turn on the RF power. When the mass flow of the nebulizer drops near zero, turn the power control knob clockwise until the forward power reads 0.5 kw. Ignite the torch by pressing the ignitor button briefly and increase the forward power to 1.25 kw. Open the sample flow valve. Switch on the automatic forward power control and turn the power control knob clockwise until it stops.

3.2.2.1.7 Turn on the reflected power alarm. Reflected RF power meter should read 5 watts or less.

3.2.2.1.8 The instrument should warm up for at least one hour to become thermally stable before beginning plasma optimization and tuning and/or calibration. Room conditions should be between 72 and 78 °F and not exceed 80% humidity.

3.2.2.2 Daily optimation and tuning:

3.2.2.2.1 Enter the PROFILE instrument mode. Aspirate a 5 ppm Cd solution and follow the "manual" directions on the screen. Check PROFILE setting by "automatic" profile. The peak position should be less than 0.1. If the peak position is greater than 0.1, see the Troubleshooting section. Profiling should be performed prior to standardization and every four hours to minimize drift.

3.2.2.2.2 Enter the ANALYSIS mode. Aspirate a 5 ppm Cu/Mn solution and read 10 replicates. If necessary, adjust the nebulizer mass flow control to approach $\pm$ 2% of the target ratio of Cu to Mn. If the ratio is greater than 2% of the target ratio, see the Troubleshooting section. Note: a new target ratio is determined each time IECs are recalculated.

3.2.2.2.3 The instrument is now ready for calibration and sample analysis.

3.2.2.3 Daily Calibration and analysis of calibration QC:

3.2.2.3.1 An initial calibration will be performed after major instrument maintenance, instrument modification, replacement of the torch and/or mirror, or the daily calibration slope is not within acceptance criteria. See section 3.1 for preparation of initial calibration solutions.

3.2.2.3.2 A daily 2-point calibration will be performed for each element with a blank and a standard at the concentration indicated in the Table 3.2-1 (STD-x solutions). If the slope for any element is not within 10% of the slope calculated during initial calibration, the instrument is recalibrated. If the slope still fails criteria, initial calibration will be performed.

3.2.2.3.3 Reanalyze the standards used in the calibration. The concentration values must be within 5% of their respective true values or the analysis must be terminated, the problem corrected and the instrument recalibrated.

3.2.2.3.4 Flush the system with the calibration blank for at least one minute before the analysis of each sample.

3.2.2.3.5 Initial calibration verification solution(s) must be analyzed after calibration and before any samples are analyzed. All values must be within 10% of their respective true values or the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified prior to sample analyses.

3.2.2.3.6 The interference check solutions are analyzed at the beginning and end of each sample analysis run. Results must fall within 20% of the true value. If not, terminate the analysis, correct the problem, recalibrate, reverify the calibration, and reanalyze the samples.

3.2.2.3.7 Continuing calibration verification solution(s) must be analyzed, after every ten samples and at the end of the run. The measured concentrations of the elements for which calibration was performed must be within 10% of their respective true values. If the continuing calibration verification solution does not pass these criteria, reanalyze the CCV. If the CCV still fails criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified prior to continuing sample analyses. All samples run after the last acceptable CCV must be reanalyzed.

3.2.2.3.8 A continuing calibration blank is analyzed after every 10 samples and at the end of the run. Blanks are to be reported to the method detection limit. If the initial calibration blank result is greater than 3 times the standard deviation of the mean blank value, repeat the analysis two more times and average the results. If the average is less than 3 times the standard deviation of the background mean, then the data are acceptable and analyses may proceed. If the average is not within criteria, terminate the analysis, correct the problem, recalibrate and reanalyze all samples analyzed since the last acceptable CCB.

3.2.2.4 Interelement correction factors are determined annually or after any major maintenance to the instrument by the following procedure:

3.2.2.4.1 Calibrate the instrument;

3.2.2.4.2 Aspirate individual solutions of each element at a concentration equal to its upper linear range and record the "apparent concentration" values produced at each channel for the remaining elements.

3.2.2.4.3 Divide the apparent concentration of analyte by the known concentration of the interferant. This factor is then programmed into each method and will automatically be applied during analysis.

3.2.2.5 The torch height must be optimized whenever the D2 mirror and/or torch are replaced, or the indicent power and/or nebulizer gas flow rate are changed. The torch height is optimized by the following procedure:

3.2.2.5.1 Aspirate a 1 ppm Cd solution and collect intensity data at the wavelength peak at 1 mm intervals from 15 to 25 mm above the top of the work coil.

3.2.2.5.2 Repeat the above process using the calibration blank.

3.2.2.5.3 Determine the position at which the ratio of peak intensity to background (blank) is maximum.

3.2.2.6 Troubleshooting:

3.2.2.6.1 If poor precision or an intensity drop is noted, check the D2 mirror, torch injector tip, introduction system for clogs and smooth drainage. Follow the cleaning procedure outlined above and replace the nebulizer, mirror or torch if necessary.

3.2.2.6.2 If the torch will not light, check the reset buttons and circuit breakers, gas pressure and level and for leaks.

3.2.2.6.3 A service contract is maintained for the instrument. If normal maintenance and troubleshooting procedures do not correct a problem, the service technician should be called. In addition, an annual preventive maintenance visit should be scheduled with the service technician.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE

Sampling procedures are defined in the appropriate field SOPs. Dissolved metals should not be preserved until after sample filtration. Soil samples are collected in 1 pint wide-mouth mason jars. It is required that the samples be chilled to 4 deg. C (°C) immediately following sampling. Water samples are collected in 1 L acid precleaned polyethelene plastic containers and preserved to pH <2.0 with nitric acid. Cooling of water samples is not required.

4.2 CONTAINERS

Sampling containers used are wide-mouth 500 mL amber jar for soils and 1 L nitric acid rinsed polyethelene cubitainers.

4.3 STORAGE CONDITIONS

Samples are stored at 4°C. in a walk-in refrigerator for soils. Water samples are stored at room temperature.

4.4 HOLDING TIMES

The holding time for digestion and analysis is 6 months from time of sampling.

4.5 SOLUTION VERIFICATION

Verification of the calibration standard stock solution is performed by analysis of a reference solution which is analyzed with every run. The reference solution is a solution of known concentration prepared from stock standards that were purchased from a different manufacturer than those stock standards from which the calibration standards were prepared.

Verification of the daily control spike stock solutions will be performed within one week prior to use for control spikes. Confirmation can occur by obtaining acceptable control spike recoveries (100 ± 10%) for high spike control spikes digested within one week of current spiking or direct analysis of a dilution of the stock solution within one week prior to spiking.

5.0 DIGESTION AND ANALYSIS PROCEDURE

5.1 DIGESTION PROCEDURE FOR SOILS

The method presented follows SW-846 Method 3050 A representative 1 to 2 gram (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with hydrochloric acid. A separate aliquot of sample is dried for a total solids determination for calculation of results on a dry weight basis.

5.1.1 Soil/Sediment Samples Digestion Procedure (SW-846/3050):

5.1.1.1 Obtain and/or prepare the required quality control samples for digestion (see next section titled Soil digestion quality control samples).

5.1.1.2 Mix the sample thoroughly to achieve homogeneity. Weigh directly into a beaker or erlenmeyer flask, a 1 to 2 g aliquot of sample to the nearest 0.0001 g. For samples with low percent solids a larger sample size may be necessary.

5.1.1.3 Add 10 mL of 1+1 HNO_3 and mix the slurry. The sample is covered with a watch glass and refluxed on a hot plate at 95°C for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.

5.1.1.4 Allow the sample to cool and add 2 mL Type II water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool.

5.1.1.5 Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than a total 10 mL of 30% H_2O_2.

5.1.1.6 Add 5 mL conc. HCl and 10 mL Type II water, return the beaker to the hot plate and reflux for an additional 15 min. without boiling. Remove the beaker and allow the sample to cool. Wash down the beaker walls with Type II water and filter or centrifuge the sample to remove particulates that could clog the ICP nebulizer during analyses. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute nitric acid prior to use.

5.1.1.7 Adjust the final volume to 100 mL with Type II water. The diluted sample has an approximate acid concentration of 5% (v/v) HCl and 5% (v/v) HNO_3.

5.1.1.8 Record the prep in the ESE Prep Logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates), and the ERA standard sand lot number. Place a copy of the logbook page in the box with the digestates.

5.1.1.9 Prepare labels for the sample bottles and sample box that will contain them.

5.1.1.10 Enter the digestion date in the computer.

5.1.2 Soil Digestion Quality Control Samples:

5.1.2.1 Preparation Blank - For each analytical batch of samples prepared, preparation (method) blanks (Type II water plus reagents) are taken through the entire sample preparation and analytical processes to determine if the samples were contaminated during their preparation. Blanks are prepared at a frequency of 5% .

5.1.2.2 Unspiked,Low, and Replicate High Control Spikes - Four Laboratory Control Samples (standard matrix spike) are included with each batch of samples. These samples are spikes using the correct volume of the USAEC ICP soil spiking solution (see Table 7.1-1 for preparation) onto 0.1 g of USAEC standard soil (reported as 10 times the weight to keep target concentrations consistent with desired spike levels of 2 and 20 times the reporting limit). The correct volume is 1.0 mL for the low spike and 10.0 mL for each high spike. If the samples are to be analyzed for Tin and/or Molybdenum, 100 uL of the 1000 ppm Sn and/or Mo stock standard is also added to the two high spikes (target in the digestate will be 2.0 mg Sn and-or Mo/L). Laboratory control samples are used to determine accuracy and precision.

5.1.2.3 Matrix Spikes - Duplicate spiked environmental samples are prepared, at a frequency of 5%, with each batch of samples to be analyzed. Two 1 g aliquots of a sample are each spiked with 10 mL of ICP Matrix Spiking Solution (see Table 7.2-1). If the samples are to be analyzed for Tin and/or Molybdenum, 100 uL of the 1000 ppm Tin and/or Molybdenum stock standard is also added to the spiked samples (target in the digestate will be 1.0 ug Sn and-or Mo/mL). Duplicate spikes are used to determine precision and matrix effects.

Note: The actual number of Matrix spike QC required is rounded up to the nearest whole number, i.e., 5% = 1 QC for 1-20 samples; 2 QC for 21-40 samples, etc. The number of samples in this calculation should be installation (USAEC project) specific. Some installations define the samples requiring matrix spikes. These samples are usually tagged with orange labels. Since Matrix spike QC will be performed per batch, tagged QC spikes may be dropped when to many samples have been tagged by the field and not distributed by collection date properly.

5.2 ANALYSIS PROCEDURES FOR SOILS - SW-846/6010

5.2.1 Obtain work assignment from the group leader and get the required box of digestates, lot folder, and method summary which contains a typical run sequence.

5.2.2 Begin the daily start-up procedures and daily optimization and tuning defined in Section 3.2 for daily calibration.

5.2.3 Profile and calibrate using the standards listed in Table 3.2-1.

5.2.4 Make sure the instrument is set up and analyze the standards samples and QC with a minimum of 2 replicates per sample, making dilutions for any elements that exceed the linear range. If the relative percent difference (RPD) between the replicate readings is greater than 20% for an element whose concentration is 10 times the instrument detection limit, repeat the analysis once. If the RPD is still greater than 20%, an interference should be suspected.

5.2.5 Reanalyze the standards used in the calibration. The concentration values must be within 5% of their respective true values or the analysis must be terminated, the problem corrected and the instrument recalibrated.

5.2.6 Flush the system with the calibration blank for at least one minute before the analysis of each sample.

5.2.7 Initial calibration verification solution(s) (ICV-19 and ICV-7) must be analyzed after calibration and before any samples are analyzed. All values must be within 10% of their respective true values or the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified prior to sample analyses.

5.2.8 The interference check solutions (ICS-A and ICS-AB) are analyzed at the beginning and end of each sample analysis run. Results must fall within 20% of the true value. If not, terminate the analysis, correct the problem, recalibrate, reverify the calibration, and reanalyze the samples.

5.2.9 A method blank (or preparation blank) must be carried through all sample preparation procedures at a frequency of 5%. The method blank is analyzed prior to the analysis of samples. The method blank fails criteria if the results are greater than 2 times the method detection limit or the project-specific detection limit. If the method blank fails criteria, all samples prepared with the method blank must be redigested and the newly prepared samples analyzed or an appropriate explanation provided as to why the data should be acceptable. For water samples the method blank and the unspiked control sample is the same sample.

5.2.10 The unspiked control sample and the three laboratory control samples (one low and replicate high standard matrix spikes). The measured concentrations of the elements for which calibration was performed must be within the decision limits of their respective true values (see control charts). If the standard matrix spike(s) fail criteria, the analysis is terminated and the samples redigested and reanalyzed or an appropriate explanation must be provided as to why the original samples should be acceptable.

5.2.11 Run samples, matrix spikes, serial dilution samples and analytical spikes to finish the ten spaces before CCV/CCB samples are required.

5.2.12 Continuing calibration verification solution(s) (CCV-1) must be analyzed, after every ten samples and at the end of the run. The measured concentrations of the elements for which calibration was performed must be within 10% of their respective true values. If the continuing calibration verification solution does not pass these criteria, reanalyze the CCV. If the CCV still fails criteria, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified prior to continuing sample analyses. All samples run after the last acceptable CCV must be reanalyzed.

5.2.13 A continuing calibration blank (CCB) is analyzed after every 10 samples and at the end of the run. Blanks are to be reported to the method detection limit. If the initial calibration blank result is greater than 3 times the standard deviation of the mean blank value, repeat the analysis two more times and average the results. If the average is less than 3 times the standard deviation of the background mean, then the data are acceptable and analyses may proceed. If the average is not within criteria, terminate the analysis, correct the problem, recalibrate and reanalyze all samples analyzed since the last acceptable CCB.

5.2.14 A post-digestion spike (analytical spike) must be analyzed at a frequency of 5% Spike recoveries for all elements should fall within 75% to 125%, inclusive. If the spike is not recovered within the specified limits, a matrix effect should be suspected (5 mL sample to 5mL CCV solution).

5.2.15 The ICP serial dilution analysis (a 1+4 or 1:5 dilution of a prepared sample) must be analyzed with each batch of 20 or fewer samples of the same matrix type taken from the same project. If the analyte concentration in the sample is sufficiently high (minimally a factor of 10 above the instrument detection limit after the sample has been diluted), an analysis of the 1+4 dilution should agree within 10% of the measured concentration in the undiluted sample. If the results do not fall within this criteria, a chemical or physical interference should be suspected.

5.2.16 The method summary contains an outline of a typical ICP run sequence. Acceptance criteria is included for each step in the procedure section and in the run sequence. If an analysis fails criteria and reanalysis can not be performed, document the problem and consult your supervisor.

6.0 CALCULATIONS

The ICP is internally calibrated based on the daily calibration and the instrument provides extract concentration units in ug/mL. An ascii file of the instrument printout is read by an upload program in the CLASS™ (Chemical Laboratory Analysis Scheduling System) is ESE's computerized data management system and the ug/mL values are stored in the ESE data batch for each properly coded sample and QC. For soils the digestion weight and final extract volume are entered from the digestion logbook. Percent moisture for each sample is accessed from the ESE data batch for actual analyses and stored in the batch. Final ug/g dry weight results are calculated by the following equation:

$$\text{Conc, dry (ug/g)} = \frac{\text{Conc.in digestate (ug/mL) x Digestate vol.(mL)}}{\text{Wet weight of sample (g) x \% solids}}$$

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SPIKES FOR SOILS

The USAEC ICAP soil spike solution is prepared (see Table 7.1-1) by adding the indicated volumes of stock solutions to a 1000 mL volumetric flask containing distilled water and 200 mL of concentrated HCl and then diluting to volume with distilled water. A low level and replicate high level daily control spikes are prepared by adding 1.0 mL for the low spike and 10.0 mL for each high spike of the USAEC ICAP soil spiking solution to 0.1 g of USAEC Standard Soil (0.1 g is used instead of 1 g because the variability of the background concentration of several elements will mask the low spike levels; 10 times the actual weight measured will be used for calculation purposes to allow target concentrations to be within the desired values for the method). The control spikes are digested and analyzed according to Sections 5.1 and 5.2, respectively.

7.2 MATRIX SPIKE SOLUTION FOR SOILS

An aliquot of each stock standard (as outlined in Table 7.2-1) is added to a 1000 mL volumetric flask containing type II water and 200 mL concentrated HCl and then diluted to volume with type II water. This solution is prepared fresh every 33 days. The manufacturer, lot number and expiration date for each stock solution are entered in the standard prep logbook. Typically 5.0 mL of spiking solution is added to 50 mL of aqueous solutions and 10.0 mL is added to soil preps which have a final volume of 100 mL. The target concentrations in the digestate are listed in the above table.

Table 7.1-1. Preparation of USAEC ICP Soil Spike Solution and Target Control Spike Concentrations.

Element	Stock Conc. (mg/L)	Volume Added (mL)	ICAP Spike Solution Conc. (mg/L)	Low Spike (SP1) Target (ug/g)	High Spike (SP2, SP3) Target (ug/g)
Aluminum*	10,000	0.8	8	8.0	80.0
Antimony	1,000	10	10	10	100
Arsenic	1,000	20	20	20	200
Barium*	1,000	5	5	5.0	50.0
Beryllium	1,000	1	1	1	10
Boron	1,000	10	10	10	100
Cadmium	1,000	1	1	1	10
Calcium*	10,000	2	20	20	200
Chromium	1,000	2	2	2	20
Cobalt	1,000	4	4	4	40
Copper	1,000	1	1	1	10
Iron*	10,000	0.9	9	9	90
Lead	1,000	10	10	10	100
Magnesium*	10,000	1	10	10	100
Manganese*	1,000	1	1	1	10
Molybdenum	1,000	2	2	2	20
Nickel	1,000	3	3	30	300
Potassium*	10,000	11	110	110	1,100
Selenium	1,000	20	20	20	200
Silver	1,000	1	1	1	10
Sodium*	10,000	2	20	20	200
Thallium	1,000	20	20	20	200
Tin	1,000	10	10	10	100
Vanadium	1,000	2	2	2	20
Zinc	1,000	10	10	10	100

* These are not control analyses.

Table 7.2-1. Preparation of Soil ICP Matrix Spike Solution.

Element	Stock Conc. (mg/L)	Volume Added (mL)	Final conc. (mg/L)	Target in Digestate (mg/L)
Aluminum	10,000	2.0	20.0	2.0
Antimony	1,000	5.0	5.0	0.5
Arsenic	1,000	20.0	20.0	2.0
Barium	1,000	20.0	20.0	2.0
Beryllium	1,000	0.5	0.5	0.05
Cadmium	1,000	0.5	0.5	0.05
Calcium	10,000	10.0	100.0	10.0
Chromium	1,000	2.0	2.0	0.2
Cobalt	1,000	5.0	5.0	0.5
Copper	1,000	2.5	2.5	0.25
Iron	10,000	1.0	10.0	1.0
Lead	1,000	5.0	5.0	0.5
Magnesium	10,000	10.0	100.0	10.0
Manganese	1,000	5.0	5.0	0.5
Nickel	1,000	5.0	5.0	0.5
Potassium	10,000	10.0	100.0	10.0
Selenium	1,000	20.0	20.0	2.0
Silver	1,000	0.5	0.5	0.05
Sodium	10,000	10.0	100.0	10.0
Thallium	1,000	20.0	20.0	2.0
Vanadium	1,000	5.0	5.0	0.5
Zinc	1,000	5.0	5.0	0.5

7.3 CONTROL CHARTS

The control charts are designed to monitor laboratory control situations which are generally tighter than method performance acceptance criteria. Therefore the burden is on the analyst and the laboratory to understand their systems and required action limits in order to observe trends with assistance from the control charts and provide sufficient explanations and corrective actions when trends or outside control limit conditions occur in order for an analytical lot to be considered acceptable. Acceptance is usually determined from decision limits which are generally outside control chart limits because control chart limits (especially for replicate high spikes) ignore day to day variability. Therefore control limits are tight compared to typical standard deviation charts when within day variability of replicates is tighter than normal day to day variability. This type of chart is useful because it forces the question to be asked: "Can daily calibration be controlled more closely?". If the answer is no then alternative decision limits become more important and trends need to be reviewed in relation to the alternate limits. Control charts and corrective action explanations are reviewed summarized and provided weekly by Project Management and QA Staff to USAEC for acceptance of a Lot.

The USAEC control chart program requires input for analysis date, lot name, target and found results for each control spike.

8.0 REFERENCES

U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects, May 1993.

Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

Federal Register, Vol. 44, No. 233, 1979. Inductively Coupled Plasma (ICP) Optical Emission Spectroscopic Method for Trace Element Analysis of Water and Wastes.

EPA Method 3005 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

EPA Method 3050 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

EPA Method 6010 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

Federal Register - Volume 4 Number 136, Appendix B.

9.0 APPENDICES

9.1 ORGANIZATION FOR LOT FOLDER - see ATTACHMENT 1

9.2 METHOD SUMMARIES FOR LOT FOLDER - see ATTACHMENT 2

9.3 INITIAL MDL RESULTS TO SUPPORT REPORTING LIMITS - see ATTACHMENT 3

ATTACHMENT 1
ORGANIZATION FOR LOT FOLDER

TABLE OF CONTENTS — METALS

A. TRANSMITTAL DOCUMENTS
(to be supplied by Information Services)

______1. Army Data Review Form
______2. IRDMS Transfer File
______3. Results of IRDMS Record and Group Check

B. ANALYST DOCUMENTS

______1. Method Summary (supplied by Information Services)
______2. ESE Data Batch Report, with:
a. Analyst Signature
b. Computer Checklist
c. Manual Checklist
d. Example Calculation
______3. Completed Control Chart and Comment/Corrective Action Form
______4. Copies of Instrument Logbook Pages (with analytical conditions)
______5. Raw Data, with:
a. Responses (emission/area counts, peak heights, etc.)
b. Calibration Curve
c. Changes made properly and initialed
______6. Copies of Sample Extract/Prep Logbook Pages
______7. Chain-of-Custody and Possession Records
a. Field Chain-of-Custody Sheets (supplied by Info. Services)
b. Laboratory Subsample Chain-of-Custody

C. APPENDIX
______1. Preliminary Data, Unused Data (if applicable)
______2. Laboratory Coordinator and QA Review Files
______3. Validation File in USATHAMA Format

Note: each of the above documents should be numbered and placed in the lot folder in the order indicated.

ATTACHMENT 2
METHOD SUMMARIES FOR LOT FOLDERS

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.:	Soils & Sediments by ICAP	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC Soil Spike Solutions - see table 7.1-1 and 7.2-1 for preparation.
2. Prepare quality control samples:
   a. Reagent blank - type I water plus reagents only.
   b. Method blank (MB) - 0.1 g standard soil plus reagents.
   c. Low Spike (SP1) - add 1.0 mL of spike solution to 0.1 g standard soil.
   d. High Spike (SP2, SP3) - add 10 mL of spike solution to 1-0.1 g portions of standard soil. If the samples are to be analyzed for Tin and/or Molybdenum, 100 uL of the 1000 ppm Sn and/or Mo stock standard is also added to the two high spikes (target in the digestate will be 2.0 mg Sn and-or Mo/L).
   c. Matrix Spikes (SPM1, SPM2) - Two 1 g aliquots of a sample are each spiked with 10 mL of ICP Matrix Spiking Solution (see Table 7.2-1). If the samples are to be analyzed for Tin and/or Molybdenum, 100 uL of the 1000 ppm Tin and/or Molybdenum stock standard is also added to the spiked samples (target in the digestate will be 1.0 ug Sn and-or Mo/mL). Duplicate spikes are used to determine precision and matrix effects.

DIGESTION PROCEDURE:

1. Mix the sample thoroughly. Weigh directly into a beaker or erlenmeyer flask, a 1-2 g aliquot of sample to the nearest 0.0001 g. For samples with low % solids a larger weight may be necessary.
2. Add 10 mL of 1+1 HNO_3 and mix the slurry. The sample is covered with a watch glass and refluxed on a hot plate at 95°C for 10-15 minutes without boiling. Cool, add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.
3. Cool and add 2 mL Type II water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool.
4. Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or general sample appearance is unchanged. Do not add more than a total 10 mL of 30% H_2O_2.
5. Add 5 mL conc. HCl and 10 mL Type II water, return the beaker to the hot plate and reflux for an additional 15 min. without boiling. Remove the beaker and allow the sample to cool. Wash down the beaker walls with Type II water and filter or centrifuge the sample to remove particulates that could clog the ICP nebulizer during analyses. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute nitric acid prior to use.
5. Adjust the final volume to 100 mL with Type II water. The diluted sample has an approximate acid concentration of 5% (v/v) HCl and 5% (v/v) HNO_3.
6. Record the prep in the ESE Prep Logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates), and the ERA standard sand lot number. Place a copy of the logbook page in the box with the digestates.
7. Prepare labels for the sample bottles and sample box that will contain them.
8. Enter the digestion date in the computer.

Number	TITLE	QC REFERENCE
USAEC No.:	Soils & Sediments by ICAP	USAEC/SW846

INSTRUMENT ANALYSIS:

1.. Optimize, profile and calibrate using the standards listed in Table 3.2-1.
2. Analyze the standards samples and QC with a minimum of 2 replicates per sample, making dilutions for any elements that exceed the linear range. If the relative percent difference (RPD) between the replicate readings is greater than 20% for an element whose concentration is 10 times the instrument detection limit, repeat the analysis once. If the RPD is still greater than 20%, an interference should be suspected.
3. Reanalyze the standards used in the calibration. Values must be within 5% of their respective true values or the analysis must be terminated, the problem corrected and the instrument recalibrated.
4. Flush the system with the blank for at least one minute before the analysis of each sample.
5. Analyze the ICVs. All values must be within 10% of their respective true values or the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified prior to sample analyses.
6. ICS-A and ICS-AB are analyzed at the beginning and end of each sample analysis run. Results must fall within 20% of the true value. If not, terminate the analysis, correct the problem, recalibrate, reverify the calibration, and reanalyze the samples.
7. A reagent blank is analyzed prior to the analysis of samples. If the reagent blank is greater than 2 times the method detection limit or the project-specific detection limit. All samples prepared with the reagent blank must be redigested and the newly prepared samples analyzed or an appropriate explanation provided as to why the data should be acceptable.
8. The method blank and the three laboratory control samples (one low and replicate high standard matrix spikes). The measured concentrations of the elements for which calibration was performed must be within control chart limits. If the standard matrix spike(s) fail criteria, the analysis is terminated and the samples redigested and reanalyzed or an appropriate explanation must be provided as to why the original samples should be acceptable.
9.. Analyze samples, matrix spikes.
10.. A CCV must be analyzed, after every ten samples and at the end of the run. If the CCV is not within 10% of the respective true values, reanalyze the CCV once. If the CCV still fails criteria, the instrument is recalibrated and all samples run after the last acceptable CCV reanalyzed.
11. A CCB is analyzed after every 10 samples and at the end of the run. If the CCB is greater than 3 times the standard deviation of the mean blank value, repeat the analysis two more times and average the results. If the average is less than 3 times the standard deviation of the background mean, then the data are acceptable and analyses may proceed. If the average is not within criteria, recalibrate and reanalyze all samples analyzed since the last acceptable CCB.
12. A post-digestion spike (analytical spike) must be analyzed at a frequency of 5% Spike recoveries for all elements should fall within 75% to 125%, inclusive. If the spike is not recovered within the specified limits, a matrix effect should be suspected (5 mL sample to 5mL CCV solution).
13. Do a serial dilution analysis (a 1+4 or 1:5 dilution of a prepared sample) with each batch of 20 samples. If the concentration is sufficiently high (minimally a factor of 10 above the instrument detection limit after the sample has been diluted), an analysis of the 1+4 dilution should agree within 10% of the measured concentration in the undiluted sample. If the results do not fall within this criteria, a chemical or physical interference should be suspected.

Number	TITLE	QC REFERENCE
USAEC No.:	Soils & Sediments by ICAP	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS data batch.
2. If the method blank has a response greater than the instrument detection limit, blank correction should be applied to the daily control spikes only. If the MB (or any sample with a matrix spike) has a negative response or is less than the instrument detection limit, enter the response as 0 Final.
3. Use 10X the actual standard soil weight for the method blank and control spike calculations.
4. Digestate volumes (0.1 L), weights (g) and % moisture should be supplied by CLASS. Verify the entries are correct. Responses should be uploaded in ug/L. (% Moisture for standard soil = 0.05). Include the sample %moisture summary in the data batch.
5. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.
6. Generate spike recovery/control chart data for Information Services.

Typical ICP Run Sequence for USACE ICP Soils Run -SW846

Calibration blank	
Standard 1 through Standard 5	
Rerun Standard 2 through 5	± 5%
Initial Calibration Verification (ICV-19)	± 10%
Initial Calibration Verification (ICV-7)	± 10%
Interference Check Sample (ICS-A)	± 20%
Interference Check Sample (ICS-AB)	± 20%
Preparation/Method Blank (MB)	
Unspiked Std. Soil	
Low Spike - (SP1)	see control charts*
High Spike - (SP2)	see control charts*
High Spike - (SP3)	see control charts*
Sample #1	
Sample #1 matrix spike (SPM1)	
Sample #1 matrix spike dup (SMP2)	
Sample #2	
Sample #2 serial dilution (1+4)	± 10%
Continuing Calibration Verification, CCV	± 10%
Continuing Calibration Blank, CCB	
Sample #3	
Sample #3 analytical spike	± 25%
Sample #4 through Sample #11	
Continuing Calibration Verification, CCV	± 10%
Continuing Calibration Blank, CCB	
Sample #12 through Sample #21	
Continuing Calibration Verification, CCV	± 10%
Continuing Calibration Blank, CCB	
Preparation/Method Blank (MB-2)	
Sample #22	
Sample #23	
Sample #23 matrix spike (SPM1)	
Sample #23 matrix spike dup (SMP2)	
Sample #24	
Sample #24 serial dilution (1+4)	± 10%
Sample #25	
Sample #26	
Sample #26 analytical spike	± 25%
CCV	± 10%
CCB	Sample #35
Sample #27 through 35	
ICS-A	± 20%
ICS-AB	± 20%
CCV	± 10%
CCB	

*Charts are reviewed for trends action limits are ± 30% for low spike control elements and ± 20% for high spike control elements.

ATTACHMENT 3
MDL RESULTS TO SUPPORT REPORTING LIMITS

MERCURY BY COLD VAPOR
(USAEC METHOD HGC1)

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: DETERMINATION OF MERCURY IN LIQUID WASTE BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY (CVAA) (SW846 METHOD 7470)
USAEC METHOD - HGC1 - WATER

TABLE OF CONTENTS

TITLE: DETERMINATION OF MERCURY IN LIQUID WASTE BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY (CVAAS) (SW846 MEHTOD 7470)
USAEC METHOD - HGC1 - WATER

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This ESE standard operating procedure follows EPA SW-846 protocols with minor deviations and additional quality control requirements applicable for the Class 1 analysis of mercury in liquid waste under the USAEC guidelines for implementation of ER 1110-1-263. The additional quality control requirements include the analysis of a low level and replicate high level control spikes in standard water.

1.2 GENERAL METHOD

This method involves acid digestion of an aliquot of the aqueous sample and analysis by cold-vapor atomic absorption. The cold-vapor technique is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the path of a mercury light source. The measured absorbance (peak height) is proportional to the concentration of mercury in the original sample or standard solution.

1.3 REPORTING LIMITS AND CALIBRATION RANGE

1.3.1 Method detection limits (MDL) are determined annually and verified quarterly and after any major maintenance or modification to the instrument. MDLs are calculated by the procedure outlined in 40 CFR 136, Appendix B.

1.3.2 The reporting limit for Hg in water is 0.2 ug/L. The upper reporting level is 10 ug/L. The calibration range is 0.2 to 10 ug/L.

1.4 INTERFERENCES

1.4.1 Standard matrix spikes are used to verify that the digestion procedure was appropriate.

1.4.2 Possible interference from sulfide is eliminated by the addition of potassium permanganate.

1.4.3 During the oxidation step, chlorides are converted to free chlorine which also absorbs radiation at 253.7nm. Therefore, brines and industrial effluents high in chlorines require additional permanganate (as much as 25mL) and an excsess of hydroxylamine hydrochloride (25mL). The dead air space in the BOD bottle is purged before adding stannous chloride to remove any free chlorine.

1.5 ANALYSIS RATE

One analyst can prepare and analyze approximately 30 samples in an 8-hour day.

1.6 SAFETY INFORMATION

Solutions of mercury and mercury vapor are very toxic. Digestions should only be carried out in a hood with adequate ventilation. During analysis, the instrument should be adequately ventelated. In addition, a bottle containing 25 mL potassium permanganate and 25 mL DI should be attached to the outlet side of the mercury analyzer, as an absorbing medium for the mercury vapor.

2.0 APPARATUS AND CHEMICALS

2.1 HARDWARE/GLASSWARE

2.1.1 Biochemical oxygen demand (BOD) bottles 300-milliliter (mL).

2.1.2 Class A volumetric flasks (2000-mL, 1000-mL and 100-mL).

2.1.3 Class A volumetric pipets (10-mL, 7-mL, 5-mL, and 2-mL).

2.1.4 Adjustable Eppendorf pipet, 1000 uL, with disposable tips.

2.1.5 Hot water bath capable of heating at 95°C.

2.1.6 Disposable beakers (10 mL).

2.1.7 Nalgene dispenser bottles (500 mL).

2.2 INSTRUMENTATION

2.1.1 Analysis is performed using a Perkin-Elmer Model MAS 50B Mercury Analyzer System or a Buck Scientific Model 400 Mercury Analyzer.

2.2.2 PARAMETERS
Wavelength: 253.7 nanometers (nm),
Sample aliquot: 100 mL.

2.3 REAGENTS AND SARMS

2.3.1 ASTM Type I water.

2.3.2 Sulfuric acid (concentrated, trace metals-grade);

2.3.3 Nitric acid (HNO_3) (concentrated, trace metals grade);

2.3.4 Potassium Permanganate, 5%: 100 g of potassium permanganate is dissolved in type I water and diluted to volume in a 2000 mL volumetric flask. This solution expires one year after the preparation date.

2.3.5 Potassium Persulfate, 5%: 100 g of potassium persulfate is dissolved in type I water and diluted to volume in a 2000 mL volumetric flask. This solution expires one year after the preparation date.

2.3.6 Sodium Chloride-Hydroxylamine Hydrochloride solution: 120 g of sodium chloride and 120 g of hydroxylamine hydrochloride are dissolved in type I water and then diluted to volume in a 1000 mL volumetric flask. This solution expires one year after the preparation date.

2.3.7 Stannous Chloride solution: 100 g stannous chloride is dissolved in type I water, 14 mL conc. H_2SO_4 added and then diluted to volume in a 1000 mL volumetric flask. This solution expires one year after the preparation date.

2.3.8 Hg stock solutions: Purchased 10 milligram-per-liter (mg/L) certified solution from two different sources or lots. The manufacturer, lot number, date received and expiration date are recorded in the preparation and instrument logbooks. Certificates of analysis are required for all stock solutions and are kept on file in the purchasing department.

2.3.9 Only use reagents "suitable for mercury determinations".

2.4 ANALYTES

The Chemical Abstract Service (CAS) number for mercury in waters is 7439-97-6. The molecular weight of Hg is 200.59, the melting point is -39 degrees Celsius (°C), and the boiling point is 357 °C.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

3.1.1 100 ug/L Mercury standard/CCV solution: using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L mercury stock solution is transferred to a 100 mL volumetric flask, 1.0 mL conc. HNO_3 added and then diluted to volume with type I water. This solution is prepared fresh, daily.

3.1.2 Standard preparation: Transfer 0.0, 0.2, 0.5, 1.0, 5.0, 7.0 and 10-mL aliquots of the 100 ug/L mercury standard/CCV solution to a series of 300-mL BOD bottles. Add enough type II water to each bottle to make a final volume of 100 mL. The concentrations for these standards are 0.2, 0.5, 1.0, 5.0, 7.0 and 10.0 ug/L. Add reagents to each bottle and heat in the same manner as the samples (Section 5.1).

3.2 INSTRUMENT CALIBRATION

3.2.1 Instrument is optimized according to manufacturers instructions with the conditions described in Section 2.2, and the calibration standards are analyzed. The analyst will construct a standard curve for Hg by plotting concentration (ug/L) versus response for the calibration standards. One reference standard is analyzed at the beginning of each analysis. If the reference is not within the calibration standards are prepared again and reanalyzed.

3.2.2 VERIFICATION OF CALIBRATION DATA

After analyzing the standards (i.e., one blank and six standards), the data are tabulated and graphed. The curve is verified with an Initial Calibration Verification Solution. A criteria of +/- 20% has been set.

3.2.3 CONTINUING CALIBRATION CHECKS

After every ten samples and at the end of each day's analyses, the blank and mid-standard (5.0 ug/L Hg) are reanalyzed. If the measured concentration for these standards is not $\pm$ 20% of the true value, the instrument is recalibrated and all samples since the last acceptable calibration check are reanalyzed.

3.3 DAILY CALIBRATION

Daily calibration and initial calibration curve and QC checks will be performed as stated in Section 3.1.

4.0 SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Water samples for metals analysis must be preserved to a pH < 2.0 with nitric acid. Samples do no need to be maintained in a temperature-controlled room at 4 degrees Celsius. Refer to project work plan for specific sample collection procedures.

4.2 SAMPLING CONTAINERS

Environmental water samples are collected nitric acid rinsed polyethylene containers.

4.3 STORAGE CONDITIONS

Samples are shipped and stored in the laboratory at room temperature. Samples may be shipped cold if they are in the same cooler as other sample fractions.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is twenty-eight days.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. The stock is verified during its shelflife by analysis of the 100 ug/L work spike solution. Since the working spike solution is made fresh daily, no verification prior to spiking can occur.

5.0 PROCEDURE

5.1 SAMPLE AND CHECK SAMPLE PREPARATION

5.1.1 Sample preparation: Transfer a 100 mL or an aliquot diluted to 100 mL of the sample to a 300-mL BOD bottle. Add 5 mL conc. H2SO4 and 2.5 mL conc. HNO3. Add 15 mL of potassium permanganate solution to each bottle. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of potassium pursulfate to each bottle and heat for 2 hours in a water bath at 95 C. Cool bottles.

Record the initial and final water bath temperature in the sample prep logbook.

5.1.2 ICV preparation: Transfer 100 mL of a reference to a 300 mL BOD bottle and add reagents and heat in the same manner as samples (Section 5.1). Do not add additional type I water.

5.1.3 Continuing Calibration Verification (CCV) preparation: Transfer 5.0 mL of the 100 ug/L mercury standard/CCV solution to a series of 300-mL BOD bottles. Add 95 mL type I water. Prepare enough CCV bottles to analyze one after every 10 samples. Add reagents to each bottle and heat in the same manner as the samples (Section 5.1).

5.1.4 Continuing Calibration Blanks (CCB): Transfer 100 mL type I water to a series of BOD bottles. Prepare sufficient blanks to analyze one after every 10 samples. Add reagents to each bottle and heat in the same manner as the samples (Section 5.1).

5.1.5 Method (preparation) blank: Transfer 100 mL of Type I water to a 300 mL BOD bottle. Add reagents and heat in the same manner as the samples (Section 5.1).

5.1.6 Laboratory control samples (standard matrix spikes): Transfer 100 mL of Type I water to the three BOD bottles for each required control spike. Add the appropriate spike amounts defined in Section 7.2 of the 80 ug/L mercury spike solution (0.5 mL for the low spike and 5.0 mL for each replicate high spike). Add reagents to each bottle and heat in the same manner as the samples (Section 5.1)

5.1.7 Sample matrix spikes and duplicate (when required): Transfer a second and third 100 mL aliquot of the sample chosen or defined for MS/MSD analysis to a BOD bottle. Add 5.0 mL of the 80 ug/L mercury spike solution. Add reagents and heat in the same manner as the samples (Section 5.1).

5.2 ANALYSIS PROCEDURES

5.2.1 Allow the analyzer to warm up for approximately 30 minutes before beginning analysis. Add 6 mL hydroxylamine hydrochloride to each standard to decolorize the solution. Wait 30 seconds. Add 5 mL of the stannous chloride solution and immediately attach the bottle to the aeration apparatus. As soon as the recorder pen levels off and starts to return to the baseline, place the aerator in a BOD bottle containing approximately 50 mL type I water and 10 mL hydroxylamine hydrochloride. When the recorder pen has returned to the baseline, analyze the next standard.

A typical run log is provided in Attachment 3. QC and samples are analyzed in the same manner as the standards.

5.2.2 ICV analysis: If the recovery is not within 20 % of the true value, repeat the analysis once. If the ICV is still not within criteria, recalibrate.

5.2.3 Method (preparation) blank analysis: If the concentration is greater than the instrument detection limit, the samples should be digested again or adequate explanation provided as to why the original samples should be acceptable.

5.2.4 Laboratory Control Sample (unspiked and spiked USAEC standard water) analysis: If the recovery for these samples is not within the established historical limits, the samples should be digested again, or adequate explanation provided as to why the original samples should be acceptable.

5.2.5 If the concentration is greater than the instrument detection limit, the samples should be digested again or adequate explanation provided as to why the original samples should be acceptable.

5.2.6 Sample analysis: Analyze the samples in the same manner as the standards. Additional hydroxylamine hydrochloride may be necessary if excess potassium permanganate was added. If the sample is high in chlorides, the dead air space must be purged before adding the satnnous chloride. If the sample peak height is greater than the peakheight for the highest standard, the sample must be diluted, redigested and reanalyzed.

5.2.7 Sample matrix spikes: If the recovery for these samples is not within the established historical limits, a matrix intereference should be suspected.

5.2.8 CCV analysis: Analyze a CCV after every 10 samples in the same manner as the standards. If the CCV is not within 20% of the true value, repeat the analysis once. If the CCV is still not within criteria, the instrument should be recalibrated and any samples analyzed since the last acceptable CCV redigested and reanalyzed.

5.2.9 CCB analysis: Analyze a CCB after every CCV. if the CCB is greater than the instrument detection limit, repeat the analysis once. If the CCB is still high, the instrument should be recalibrated and any samples analyzed since the last acceptable CCB should be redigested and reanalyzed.

6.0. CALCULATIONS

Prepare a curve by plotting the micrograms-per-liter of Hg present in the standards versus the peak height response of the calibration standards. Determine the peak height response of the sample aliquot from the chart and calculate the corresponding ug/L Hg value from the standard curve.

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF STOCK SPIKING SOLUTIONS

Working spike solution (80 ug/L Hg): using a calibrated Eppendorf pipet, 0.80 mL of the 10 mg/L Hg stock solution (different than the one used to prepare the standard/CCV solution) is transfered to a 100 mL volumetric flask, 1.0 mL conc. HNO_3 added and then diluted to volume with deionized water (prepare fresh daily).

7.2 PREPARATION OF DAILY CONTROL SPIKE SAMPLES

The following daily control spike samples are prepared by adding the following volumes of the Hg spiking solution (as prepared in Section 7.1) to 100 mL of ASTM Type I water. Each control spike is digested and analyzed as described in Section 5.0.

Daily Control Spike Sample Prepared	Volume (mL) of Hg Spiking Solution Spiked to 100 mL	Concentration of Control Spike (ug/L)
Blank	0	0
Low	0.5	0.4
High	5.0	4.0
High	5.0	4.0

7.3 MATRIX SPIKE, MATRIX SPIKE DUPLICATES (MS/MSD)

MS/MSD analyses will be performed when required for USAEC projects. The spike level will be the sampe as the high spike defined in Section 7.2.

7.4 CONTROL CHARTS

The USAEC control chart program requires input for analysis date, lot name, target and found results for each control spike.

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot,
2. Difference between the two high concentration spiked QC samples in each lot.
3. Three-point moving average percent recovery for the low level spike in each lot, and
4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projects, May 1992.

8.2 U.S. Environmental Protection Agency Test Methods for Evaluating Solid Waste. SW846, 3rd Edition, Method 7470. September, 1986.

8.3 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.4 Federal Register, Vol. 40, No. 136, Appendix B, "Definitions and Procedures for determination of the Method Detection Limit", July 1, 1990.

9.0 APPENDICES

9.1 Method Summary

9.2 Typical CVAA Run Sequence

9.3 MDL Study

ATTACHMENT 1 - METHOD SUMMARY

LOT FOLDER ORGANIZATION - the following items will be numbered and placed in the lot folder in the order indicated:

A. ANALYST DOCUMENTS

1. Method Summary (supplied by Information Services)

2. ESE Data Batch Report, with:
   a. Analyst Signature
   b. Computer Checklist
   c. Manual Checklist
   d. Example Calculation

3. Completed Control Chart and Comment/Corrective Action Form

4. Copies of Instrument Logbook Pages with Analytical Conditions

5. Raw Data, with:
   a. Responses (emission/area counts, peak heights, etc.)
   b. Calibration Curve
   c. Changes made properly and initialed.

6. Copies of Sample Extraction/Preparation Logbook Pages

7. Chain-of-Custody and Possession Records
   a. Field Chain-of-Custody Sheets (supplied by Information Services)
   b. Laboratory Subsample Chain-of-Custody

8. Preliminary Data, Unused Data (if applicable)

Lot No.:__________

SUMMARY OF METHOD

NUMBER	TITLE	QC REFERENCE
	Analysis of Mercury in Water by CVAA	USAEC

SAMPLE PREPARATION:

1. Transfer 100 mL or an aliquot diluted to 100 mL of the water sample to a 300 mL BOD bottle.
2. To each BOD bottle, add 5.0 mL conc. $H2SO_4$ and 2.5 mL conc. HNO_3.
3. Add 15 mL potassium permanganate to each sample. Repeat this process if the purple color does not remain for at least 15 min.
4. Add 8 mL of potassium persulfate to each bottle and heat for 2 hours.
5. Record the initial and final water bath temperature in the sample prep logbook.

QC SAMPLE PREPARATION:

1. Method blank - Transfer 100 mL of Type I water to a BOD bottle. Proceed in the same manner as the samples.
2. Low spike - Transfer 100 mL of Type I water to a BOD bottle, add 0.5 mL of a 80 ug/L mercury spike solution, proceed in the same manner as the samples. [target = 0.4 ug/L)]
3. High spike - Transfer two 100 mL portions of Type I water to BOD bottles, add 5.0 mL of a 80 ug/L mercury spike solution, proceed in the same manner as the samples. [target = 4.0 ug/L)]
4. Sample matrix spikes - add 5.0 mL of the 80 ug/L mercury spike solution to a 100 mL aliquot of sample in a BOD bottle and proceed in the same manner as the samples [target = 4.0 ug/L].
5. ICV solutions - transfer 100 mL of an EPA certified reference to a 300 mL BOD bottle and proceed in the same manner as the samples. Prepare two references. NOTE: do not add additional DI.

STANDARD PREPARATION:

1. Transfer 0.0, 0.2, 0.5, 1.0, 5.0, 7.0, and 10.0 mL aliquots of a 100 ug/L mercury solution (from a different stock than the one used for the spikes) to a series of 300 mL BOD bottles. Add deionized water to each bottle to total approx. 10 mL and proceed in the same manner as the samples.
   [standard concentrations = 0.0, 0.2, 0.5, 1.0, 5.0, 7.0 and 10.0 ug/L]

INSTRUMENT ANALYSIS:

1. Instrument: Buck 400 or Perkin-Elmer MAS50B mercury analyzer system. Allow approx. 30 min. warm-up.
2. Add 6 mL sodium chloride-hydroxylamine hydrochloride to each BOD bottle to reduce the excess permanganate (additional hydroxylamine may be necessary if excess permanganate was added).
3. Calibration: add 5 mL stannous chloride and immediately attach to the aeration apparatus. As soon as the recorder pen levels off and starts to return to the baseline, place the aerator in a BOD bottle containing approx. 50 mL deionized water. When the recorder pen has returned to the baseline, analyze the next standard.
4. Analyze the references, spikes, and samples in the same manner as the standard. If the sample is high in chlorides, the dead air space must be purged before adding the stannous chloride. If a sample concentration is greater than 10 ug/L the sample must be redigested and analyzed again using a smaller aliquot diluted to 100 mL.
   NOTE: if a samples is not repreped on the same day as the first prep, the sample must be assigned to a new lot folder.
5. QC: analyze a reference immediately after calibration, a 5.0 ug/L standard and blank after every 10 samples at the end of the run. Recoveries for the standards and references must be $\pm$ 20%.
6. Responses are recorded on a strip chart recorder.

ESE DATA ENTRY

1. Enter calibration standards and calculate the sample concentration in CLASS.
2. If the method blank has a response greater than the instrument detection limit, blank correction should be applied the the daily spikes only. For the method blank or any samples with SPMs, if the response is less than the instrument detection limit, report the result as "0 Final".
3. Responses and targets must be entered in ug/L.

ATTACHMENT 2 -
TYPICAL RUN SEQUENCE

Typical Mercury Run Sequence
USATHAMA/SW846 Samples

Blank	
Standard 1 (0.2 ug/L)	
Standard 2 (0.5 ug/L)	
Standard 3 (1.0 ug/L)	
Standard 4 (5.0 ug/L)	
Standard 5 (7.0 ug/L)	
Standard 6 (10.0 ug/L)	
Initial calibration verification - ICV (reference)	± 20%
Method blank (MB)	
Low spike (SP1)	
High spike (SP2)	
High spike (SP3)	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike dup	
Sample #2	
Sample #3	
Sample #4	
CCV (5.0 ug/L)	± 20%
Continuing calibration blank - CCB	
Sample #5	
.	
.	
Sample #14	
CCV (5.0 ug/L)	± 20%
CCB	
Sample #15	
.	
.	
Sample #21	
Sample #21 matrix spike	
Sample #21 matrix spike dup	
Sample #22	
CCV (5.0 ug/L)	± 20%
CCB	
Sample #23	
.	
.	
Sample #30	
CCV (5.0 ug/L)	± 20%
CCB	

ATTACHMENT 3 -
METHOD DETECTION LIMIT STUDY

CVAA Instrument & Method Detection Limits
JANUARY 1993

Element	Spike Conc. (ug/L)	Day 1 Response (ug/L)	Day 1 SD (ug/L)	Day 2 Response (ug/L)	Day 2 SD (ug/L)	Day 3 Response (ug/L)	Day 3 SD (ug/L)	IDL (ug/L)	Reported IDL (ug/L)	Unspiked Response (ug/L)	Spiked Response (ug/L)	MDL (ug/L)	Reported MDL (ug/L)
Mercury	0.5	0.49	0.04	0.56	0.04	0.41	0.04	0.12	0.15	0.00	0.49	0.12	0.20
BUCK 400		0.53		0.60		0.37					0.53		
		0.45		0.56		0.37					0.45		
		0.41		0.56		0.41					0.41		
		0.45		0.60		0.41					0.45		
		0.45		0.52		0.49					0.45		
		0.45		0.48		0.45					0.45		

Reference: CLP390 (ILM01.0) & 40 CFR 136, App. B/SW846

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: DETERMINATION OF MERCURY IN SOLID OR SEMI-SOLID WASTE BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY (CVAA) (SW846 METHOD 7471)
USAEC METHOD - HGC1 - SOIL

TABLE OF CONTENTS

TITLE: DETERMINATION OF MERCURY IN SOLID OR SEMI-SOLID WASTE BY COLD VAPORATOMIC ABSORPTION SPECTROSCOPY (CVAAS) (SW846 MEHTOD 7471)
USAEC METHOD - HGC1 - SOIL

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This ESE standard operating procedure follows EPA SW-846 protocols with minor deviations and additional quality control requirements applicable for the Class 1 analysis of mercury in solid or semi-solid wastes under the USAEC guidelines for implementation of ER 1110-1-263. The additional quality control includes the analysis of one low spike and replicate high spikes in USAEC standard soil.

1.2 GENERAL METHOD

1.2.1 This method involves acid digestion of an aliquot of the soil sample and analysis by cold-vapor atomic absorption. The cold-vapor technique is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the path of a mercury light source. The measured absorbance (peak height) is proportional to the concentration of mercury in the original sample or standard solution.

1.2.2 SW 846 Method 7471 provides two options for soil digestion: 1) aqua regia in a water bath at 95 degrees C; or 2) sulfuric and nitric acid autoclaved at 121 decrees C. EPA CLP procedures (ILM01.0) and the SW-846 water procedure (7240) allow for the use of the sulfuric and nitric acid with potassium persulfate at 95 degrees C. This deviation from SW-846 is considered minor because the digestion procedures have proven to be complete. The digestion procedure chosen is as follows: Weigh a 0.2-g portion of the sample and place in a 300-mL BOD bottle. Add 10 mL type II water, 5 mL conc. H_2SO_4 and 2.5 mL of conc. HNO_3, mixing after each addition. Heat for 2 minutes in a water bath maintained at 95°C. Cool and add 50 mL of type II water. Add 15 mL of potassium permanganate solution to each sample bottle.

Mix well and heat for 10 min. Repeat this process adding additional portions of potassium permanganate, if necessary, until the purple color persists for at least 10 minutes. Add 8 mL of potassium persulfate to each bottle and heat for 30 minutes in a water bath at 95^{0}C. Cool bottles. Add 40 mL of type I water.

1.3 REPORTING LIMITS AND CALIBRATION RANGE

1.3.1 Method detection limits (MDL) are determined annually and verified quarterly and after any major modification or maintenance to the instrument. MDLs are calculated by procedure method in 40CFR136, Appendix B.

1.3.2 The reporting limit for Hg in soil is 0.1 ug/g. The upper certified range is 5 ug/g. The calibration range is 0.2 to 10 ug/L which relates to a calibration range of 0.1 to 5.0 ug/g when 0.2 g of soil is digested to a 100 mL final volume.

1.4 INTERFERENCES

1.4.1 Standard matrix spikes are used to verify that the digestion procedure was appropriate.

1.4.2 Possible interference from sulfide is eliminated by the addition of potassium permanganate.

1.4.3 During the oxidation step, chlorides are converted to free chlorine which also absorbs radiation at 253.7nm. Therefore, brines and industrial effluents high in chlorines require additional permanganate (as much as 25mL) and an excsess of hydroxylamine hydrochloride (25mL). The dead air space in the BOD bottle is purged before adding stannous chloride to remove any free chlorine.

1.5 ANALYSIS RATE

One analyst can prepare and analyze approximately 30 samples in an 8-hour day.

1.6 SAFETY INFORMATION

Solutions of mercury and mercury vapor are very toxic. Digestions should only be carried out in a hood with adequate ventilation. During analysis, the instrument should be adequately ventilated. In addition, a bottle containing 25 mL potassium permanganate and 25 mL DI should be attached to the outlet side of the mercury analyzer as an absorbing medium for the mercury vapor.

2.0 APPARATUS AND CHEMICALS

2.1 HARDWARE/GLASSWARE

2.1.1 Biochemical oxygen demand (BOD) bottles, 300-milliliter (mL).

2.1.2 Class A volumetric flasks (2000-mL, 1000-mL and 100-mL);

2.1.3 Class A volumetric pipets (10-mL, 7-mL, 5-mL, and 2-mL);

2.1.4 Adjustable Eppendorf pipet, 1000 uL, with disposable tips;

2.1.5 Hot water bath capable of heating at 95°C.

2.1.6 Disposable beakers (10 mL).

2.1.7 Nalgene dispenser bottles (500 mL).

2.1.8 Analytical balance, capable of weighing accurately to 0.0001 grams.

2.2 INSTRUMENTATION

2.1.1 Analysis is performed using a Perkin-Elmer Model MAS 50B Mercury Analyzer System or a Buck Scientific Model 400 Mercury Analyzer.

2.2.2 PARAMETERS
Wavelength: 253.7 nanometers (nm),
Sample aliquot: 0.2 g.

2.3 REAGENTS AND SARMS

2.3.1 USAEC Standard Soil and ASTM Type I Water.

2.3.2 Sulfuric acid (concentrated, trace metals-grade);

2.3.3 Nitric acid (HNO_3) (concentrated, trace metals grade);

2.3.4 Potassium Permanganate, 5%: 100 g of potassium permanganate is dissolved in type I water and diluted to volume in a 2000 mL volumetric flask. This solution expires one year after the preparation date.

2.3.5 Potassium Persulfate, 5%: 100 g of potassium persulfate is dissolved in type I water and diluted to volume in a 2000 mL volumetric flask. This solution expires one year after the preparation date.

2.3.6 Sodium Chloride-Hydroxylamine Hydrochloride solution: 120 g of sodium chloride and 120 g of hydroxylamine hydrochloride are dissolved in type I water and then diluted to volume in a 1000 mL volumetric flask. This solution expires one year after the preparation date.

2.3.7 Stannous Chloride solution: 100 g stannous chloride is dissolved in Type I water, 14 mL conc. H_2SO_4 added and then diluted to volume in a 1000 mL volumetric flask. This solution expires one year after the preparation date.

2.3.8 Hg stock solutions: Purchased 10 milligram-per-liter (mg/L) certified solution from two different sources or lots. The manufacturer, lot number, date received and expiration date are recorded in the preparation and instrument logbooks. Certificates of analysis are required for all stock solutions and are kept on file in the purchasing department.

2.3.9 Only use reagents "suitable for mercury determinations.

2.4 ANALYTES

The Chemical Abstract Service (CAS) number for mercury in soil is 7439-97-6. The molecular weight of Hg is 200.59, the melting point is -39 degrees Celsius (°C), and the boiling point is 357 °C.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

3.1.1 100 ug/L Mercury standard/CCV solution: using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L mercury stock solution is transferred to a 100 mL volumetric flask, 1.0 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

3.1.2 Standard preparation: Transfer 0.0, 0.2, 0.5, 1.0, 5.0, 7.0 and 10-mL aliquots of the 100 ug/L mercury standard/CCV solution to a series of 300-mL BOD bottles. Add enough Type I water to each bottle to make a final volume of 100 mL. The concentrations for these standards are 0.2, 0.5, 1.0, 5.0, 7.0 and 10.0 ug/L. Add reagents to each bottle and heat in the same manner as the samples (Section 5.1).

3.2 INSTRUMENT CALIBRATION

3.2.1 The instrument is optimized according to manufacturers instructions with the conditions described in Section 2.2, and the calibration standards are analyzed. The analyst will construct a standard curve for Hg by plotting a concentration (ug/L) versus response for the calibration standards. One reference standard is analyzed at the beginning of each analysis. If the reference is not within $\pm$ 20%, the calibration standards are prepared again and reanalyzed.

3.2.2 Verification of Calibration Data

After analyzing the standards (i.e., one blank and six standards), the data are tabulated and graphed. The curve is verified with an Initial Calibration Verification Solution. A criteria of +/- 20% has been set.

3.2.3 Continuing Calibration Checks

After every ten samples and at the end of each day's analyses, the blank and mid-standard (5.0 ug/L Hg) are reanalyzed. If the measured concentration for these standards is not $\pm$ 20% of the true value, the instrument is recalibrated and all samples since the last acceptable calibration check are reanalyzed.

3.3 DAILY CALIBRATION

Daily calibration and initial calibration curve and QC checks will be performed as stated in Section 3.1.

4.0 SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Soil and sediment samples for metals analysis must be maintained in a temperature-controlled room at 4 degrees Celsius (oC). Refer to project work plan for specific sample collection procedures.

4.2 SAMPLING CONTAINERS

Environmental soil and sediment samples are collected in wide-mouth, amber-glass jars with teflon-lined lids.

4.3 STORAGE CONDITIONS

Samples are shipped and stored in the laboratory at 4° C.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is twenty-eight days.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. The stock is verified during its shelflife by analysis of the 100 ug/L work spike solution. Since the working spike solution is made fresh daily, no verification prior to spiking can occur.

5.0 PROCEDURE

5.1 SAMPLE & CHECK SAMPLE PREPARATION

5.1.1 Sample preparation: Weigh a 0.2-g portion of the sample and rinse into a 300-mL BOD bottles with 10 mL of Type I water. Add 5 mL conc. H2SO4 and 2.5 mL conc. HNO3. Heat for 2 minutes in a water bath maintained at 95 C. Cool and add 50 mL of Type I water. Add 15 mL of potassium permanganate solution to each bottle. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of potassium pursulfate to each bottle and heat for 30 minutes in a water bath at 95 C. Cool bottles. Add 40 mL of Type I water.

Record the initial and final water bath temperature in the sample prep logbook.

5.1.2 ICV preparation: Transfer 100 mL of a reference to a 300 mL BOD bottle and add reagents and heat in the same manner as samples (Section 5.1). Do not add additional Type I water.

5.1.3 Continuing Calibration Verification (CCV) preparation: Transfer 5.0 mL of the 100 ug/L mercury standard/CCV solution to a series of 300-mL BOD bottles. Add 5 mL Type I water. Prepare enough CCV bottles to analyze one after every 10 samples. Add reagents to each bottle and heat in the same manner as the samples (Section 5.1).

5.1.4 Continuing Calibration Blanks (CCB): Transfer 10 mL Type I water to a series of BOD bottles. Prepare sufficient blanks to analyze one after every 10 samples. Add reagents to each bottle and heat in the same manner as the samples (Section 5.1).

5.1.5 Method (preparation) blank: Weigh a 0.2 g portion of the USAEC standard soil and place in a 300 mL BOD bottle. Add 10 mL Type I water, add reagents and heat in the same manner as the samples (Section 5.1).

5.1.6 Laboratory control samples (standard matrix spikes): Weigh three separate 0.2 g portions of USAEC standard soil and transfer to BOD bottles. Add 5.0 mL of Type I water to each bottle and the appropriate spike amounts defined in Section 7.2 of the 80 ug/L mercury spike solution (0.5 mL for the low spike and 5.0 mL for each replicate high spike). Add reagents to each bottle and heat in the same manner as the samples (Section 5.1)

5.1.7 Sample matrix spikes and duplicate (when required): Transfer a second and third 0.2 g aliquot of the sample chosen or defined for MS/MSD analysis to BOD bottles. Add 5.0 mL of Type I water and 5.0 mL of the 80ug/L mercury spike solution to each. Add reagents and heat in the same manner as the samples (Section 5.1).

5.1.8 Reagent blank: Add 10 mL Type I water to a BOD bottle, add reagents and heat in same manner as the samples.

5.1.9 A typical run sequence is provided in Attachment 3.0.

5.2 ANALYSIS PROCEDURES

5.2.1 Allow the analyzer to warm up for approximately 30 minutes before beginning analysis. Add 6 mL hydroxylamine hydrochloride to each standard to decolorize the solution. Wait 30 seconds. Add 5 mL of the stannous chloride solution and immediately attach the bottle to the aeration apparatus. As soon as the recorder pen levels off and starts to return to the baseline, place the aerator in a BOD bottle containing approximately 50 mL Type I water and 10 mL hydrozylamine hydrochloride. When the recorder pen has returned to the baseline, analyze the next standard.

A typical run log is provided with the method summary in Attachment 1.

5.2.2 ICV analysis: If the recovery is not within 20 % of the true value, repeat the analysis once. If the ICV is still not within criteria, recalibrate.

5.2.3 Reagent blank - Analyze a CCB at the begining of the run as a reagent blank. If the concentration is greater than the instrument detection limit, the samples should be digested again or adequate explanation provided as to why the original samples should be acceptable.

5.2.4 Method (preparation) blank analysis: If the concentration is greater than the instrument detection limit, the samples should be digested again or adequate explanation provided as to why the original samples should be acceptable.

5.2.5 Laboratory Control Sample (unspiked and spiked USAEC standard soil) analysis: If the recovery for these samples is not within the established historical limits, the samples should be digested again, or adequate explanation provided as to why the original samples should be acceptable.

5.2.6 Sample analysis: Analyze the samples in the same manner as the standards. Additional hydroxylamine hydrochloride may be necessary if excess potassium permanganate was added. If the sample is high in chlorides, the dead air space must be purged before adding the satnnous chloride. If the sample peak height is greater than the peakheight for the highest standard, the sample must be diluted, redigested and reanalyzed.

5.2.7 Sample matrix spikes: If the recovery for these samples is not within the established historical limits, a matrix intereference should be suspected.

5.2.8 CCV analysis: Analyze a CCV after every 10 samples in the same manner as the standards. If the CCV is not within 20% of the true value, repeat the analysis once. If the CCV is still not within criteria, the instrument should be recalibrated and any samples analyzed since the last acceptable CCV redigested and reanalyzed.

5.2.9 CCB analysis: Analyze a CCB after every CCV. if the CCB is greater than the instrument detection limit, repeat the analysis once. If the CCB is still high, the instrument should be recalibrated and any samples analyzed since the last acceptable CCB should be redigested and reanalyzed.

6.0. CALCULATIONS

Prepare a calibration curve by plotting the micrograms-per-liter of Hg present in the standards versus the peak height response of the calibration standards. Determine the peak height response of the sample aliquot from the chart and calculate the corresponding ug/L Hg value from the standard curve. Calculate the Hg concentration in the sample by the formula:

$$\text{ug Hg/g soil sample} = \frac{\text{ug/L Hg in the aliquot x 0.1 L}}{\text{wt of soil sample in g * (100 - \%Moisture)}}$$

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF STOCK SPIKING SOLUTIONS

Working spike solution (80 ug/L Hg): using a calibrated Eppendorf pipet, 0.8 mL of the 10 mg/L Hg stock solution (different than the one used to prepare the standard/CCV solution) is transfered to a 100 mL volumetric flask, 1.0 mL conc. HNO_3 added and then diluted to volume with deionized water (prepare fresh daily).

7.2 PREPARATION OF DAILY CONTROL SPIKE SAMPLES

The following daily control spike samples are prepared by adding the following volumes of the Hg spiking solution (as prepared in Section 7.1) to 0.2 g of USATHAMA standard soil. Each control spike is digested and analyzed as described in Section 5.0.

Daily Control Spike Sample Prepared	Volume (mL) of Hg Spiking Solution Spiked to 0.2g soil	Concentration of Control Spike (ug/L)	Concentration of Control Spike (ug/g)
Blank	0	0	0
Low	0.5	0.4	0.2
High	5.0	4.0	2.0
High	5.0	4.0	2.0

7.3 MATRIX SPIKE, MATRIX SPIKE DUPLICATES (MS/MSD)

MS/MSD analyses will be performed when required for USAEC projects. The spike level will be the sampe as the high spike defined in Section 7.2.

7.4 CONTROL CHARTS

The USAEC control chart program requires input for analysis date, lot name, target and found results for each control spike.

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

The found response is corrected for unspiked standard soil concentration, when necessary, prior to calculation of the found concentration. Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot,
2. Difference between the two high concentration spiked QC samples in each lot.
3. Three-point moving average percent recovery for the low level spike in each lot, and
4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implemetation of ER 1110-1-263 for USAEC Projects, May 1993.

8.2 U.S. Environmental Protection Agency Test Methods for Evaluating Solid Waste. SW846, 3rd Edition, Method 7471. September, 1986.

8.3 USEPA Contract Laboratory Program Statement of Work for Inorganic Analysis, Document Number ILM01.0.

8.4 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.5 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit", July 1, 1990.

9.0 ATTACHMENTS

9.1 METHOD SUMMARY - See attachment 1.

9.2 TYPICAL CVAA RUN SEQUENCE

9.3 MDL STUDES

ATTACHMENT 1 - METHOD SUMMARY

LOT FOLDER ORGANIZATION - the following items will be numbered and placed in the lot folder in the order indicated:

A. ANALYST DOCUMENTS

1. Method Summary (supplied by Information Services)

2. ESE Data Batch Report, with:
   a. Analyst Signature
   b. Computer Checklist
   c. Manual Checklist
   d. Example Calculation

3. Completed Control Chart and Comment/Corrective Action Form

4. Copies of Instrument Logbook Pages with Analytical Conditions

5. Raw Data, with:
   a. Responses (emission/area counts, peak heights, etc.)
   b. Calibration Curve
   c. Changes made properly and initialed.

6. Copies of Sample Extraction/Preparation Logbook Pages

7. Chain-of-Custody and Possession Records
   a. Field Chain-of-Custody Sheets (supplied by Information Services)
   b. Laboratory Subsample Chain-of-Custody

8. Preliminary Data, Unused Data (if applicable)

Lot No.:__________

SUMMARY OF METHOD

NUMBER	TITLE	QC REFERENCE
	Analysis of Mercury in Soils by CVAA	USAEC

SAMPLE PREPARATION:

1. Weigh 0.2-g portions of the soil sample. Record the weight. Transfer sample to a 300 mL BOD bottle by rinsing weigh boat with approx. 10 mL deionized water.
2. To each BOD bottle, add 5.0 mL conc. $H2SO_4$ and 2.5 mL conc. HNO_3. Place caps on bottles and heat at 95°C for 2 min.
3. Cool. Add 50 mL deionized water.
4. Add 15 mL potassium permanganate to each sample. Mix well and heat for 10 min. Repeat this process until the purple color remains at least 10 min.
5. Cool. Add 8 mL of potassium persulfate to each bottle and heat for 30 min.
6. Cool, add 40 mL deionized water to each bottle.
7. Record the initial and final water bath temperature in the sample prep logbook.

QC SAMPLE PREPARATION:

1. Reagent blank - weigh a 0.2-g portion of the USAEC standard soil. Record weight. Proceed in the same manner as the samples.
2. Low spike - weigh a 0.2-g portion of the USAEC standard soil. Record weight. Transfer to BOD bottle, add 0.5 mL of a 80 ug/L mercury spike solution, proceed in the same manner as the samples. [target = 0.2 ug/g (0.4 ug/L)]
3. High spike - weigh two 0.2-g portions of the USAEC standard soil. Record weights. Transfer to BOD bottles, add 5.0 mL of a 80 ug/L mercury spike solution, proceed in the same manner as the samples. [target = 2.0 ug/g (4.0 ug/L)]
4. Sample matrix spikes - add 5.0 mL of the 80 ug/L mercury spike solution to a 1 g portion of sample and proceed in the same manner as the samples [target = 2.0 ug/g (4.0 ug/L)].
5. ICV solutions - transfer 100 mL of an EPA certified reference to a 300 mL BOD bottle and proceed in the same manner as the samples. NOTE: do not add additional DI.

STANDARD PREPARATION:

1. Transfer 0.0, 0.2, 0.5, 1.0, 5.0, 7.0, and 10.0 mL aliquots of a 100 ug/L mercury solution (from a different stock than the one used for the spikes) to a series of 300 mL BOD bottles. Add deionized water to each bottle to total approx. 10 mL and proceed in the same manner as the samples.
   [standard concentrations = 0.0, 0.2, 0.5, 1.0, 5.0, 7.0 and 10.0 ug/L]

INSTRUMENT ANALYSIS:

1. Instrument: Buck 400 or Perkin-Elmer MAS50B mercury analyzer system. Allow approx. 30 min. warm-up.
2. Add 6 mL sodium chloride-hydroxylamine hydrochloride to each BOD bottle to reduce the excess permanganate (additional hydroxylamine may be necessary if excess permanganate was added).
3. Calibration: add 5 mL stannous chloride and immediately attach to the aeration apparatus. As soon as the recorder pen levels off and starts to return to the baseline, place the aerator in a BOD bottle containing approx. 50 mL deionized water. When the recorder pen has returned to the baseline, analyze the next standard.
4. Analyze the references, spikes, and samples in the same manner as the standard. If the sample is high in chlorides, the dead air space must be purged before adding the stannous chloride. If a sample concentration is greater than 5 ug/g (10 ug/L), the sample must be redigested and analyzed again using a smaller aliquot diluted to 100 mL.
   NOTE: if a samples is not repreped on the same day as the first prep, the sample must be assigned to a new lot folder.
5. QC: analyze a reference immediately after calibration, a 5.0 ug/L standard and blank after every 10 samples; and at the end of the run. Recoveries for the standards and references must be $\pm$ 20%.
6. Responses are recorded on a strip chart recorder.

ESE DATA ENTRY

1. Enter calibration standards and calculate sample responses in CLASS.
2. If the method blank has a response greater than the instrument detection limit, blank correction should be applied the the daily spikes only. For the method blank or any samples with SPMs, if the response is less than the instrument detection limit, report the result as "0 Final".
3. Responses and targets must be entered in ug/L; sample weight in g; and sample volume as 0.1 L. Percent moisture for the USAEC standard soil is 0.05. Also include the % moisture summary page in the data batch.

ATTACHMENT 2 -
TYPICAL CVAA RUN SEQUENCE

Typical Mercury Run Sequence
USAEC/SW846 Samples

Blank	
Standard 1 (0.2 ug/L)	
Standard 2 (0.5 ug/L)	
Standard 3 (1.0 ug/L)	
Standard 4 (5.0 ug/L)	
Standard 5 (7.0 ug/L)	
Standard 6 (10.0 ug/L)	
Initial calibration verification - ICV (reference)	± 20%
Reagent blank (MB)	
Low spike (SP1)	
High spike (SP2)	
High spike (SP3)	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike dup	
Sample #2	
Sample #3	
Sample #4	
CCV (5.0 ug/L)	± 20%
Continuing calibration blank - CCB	
Sample #5	
.	
.	
Sample #14	
CCV (5.0 ug/L)	± 20%
CCB	
Sample #15	
.	
.	
Sample #21	
Sample #21 matrix spike	
Sample #21 matrix spike dup	
Sample #22	
CCV (5.0 ug/L)	± 20%
CCB	
Sample #23	
.	
.	
Sample #30	
CCV (5.0 ug/L)	± 20%
CCB	

October 27, 1993

ATTACHMENT 3 -
METHOD DETECTION LIMIT STUDES

October 27, 1993

CVAA Soil/Sediment MDL Study
January 1993

Element	Spike Conc. (ug/L)	Spike Conc. (ug/g)	ERA-Unspiked Response (ug/g)	ERA-Spike Response (ug/L)	ERA-Spike Weight (g)	ERA-Spike Response (ug/g)	Standard Deviation (ug/g)	ERA Soil MDL (ug/g)	AEC-Unspiked Response (ug/g)	AEC-Spike Response (ug/L)	AEC-Spike Weight (g)x10	AEC-Spike Response (ug/g)	Standard Deviation (ug/g)	AEC Soil MDL (ug/g)	Combined Reported MDL (ug/g)
Mercury	0.50	0.050	0.0000	0.45	1.0021	0.0449	0.0032	0.010	0.0000	0.49	1.0007	0.0490	0.0035	0.011	0.020
Buck 400				0.45	1.0002	0.0450				0.53	1.0012	0.0529			
				0.45	1.0010	0.0450				0.53	1.0021	0.0529			
				0.49	1.0008	0.0490				0.53	1.0017	0.0529			
				0.45	1.0024	0.0449				0.58	1.0023	0.0579			
				0.53	1.0013	0.0529				0.58	1.0013	0.0579			
				0.45	1.0029	0.0449				0.58	1.0007	0.0580			

Reference: 40 CFR 136, Appendix B (ERA Inorganic Blank Sand & AEC Standard Soil)/SW846

ARSENIC BY GFAA
(USAEC METHOD GAS1)

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **ANALYSIS OF AQUEOUS SAMPLES FOR ARSENIC BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7060)**
USAEC METHOD - GAS1 - WATER

TABLE OF CONTENTS

TITLE: **ANALYSIS OF AQUEOUS SAMPLES FOR ARSENIC BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7060) USAEC METHOD - GAS1 - WATER**

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental aqueous samples and wastes with suspended solids for arsenic (As) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Aqueous samples for GFAAS determination are digested and analyzed following EPA SW-846 Method 7060.

1.2.2 There are three deviations from the SW-846 method: a) the initial and final volume of sample digested is 50 mL instead of 100 mL, b) after digestion, the acid concentration of the samples is adjusted to 5% to match soil samples prepared by SW-846 Method 3050 and aqueous samples prepared by SW-846 Method 3020 which allows the use of a single set of standards for all preps, and c) the use of palladium nitrate as a matrix modifier instead of nickel nitrate based on the instrument manufacturer's recommendations.

1.2.3 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at twice the reporting limit and two spikes at twenty times the reporting limit will be digested and analyzed with each lot of samples.

1.2.4 A representative 50 mL aliquot of sample is prepared for analysis by refluxing on a hot plate at approximately 95°C with a mixture of nitric acid and hydrogen peroxide in a covered beaker. The digestate is then cooled, filtered and diluted to 50 mL.

1.2.5 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of light at a specific wavelength during atomization is measured and the concentration of arsenic in the sample is calculated based on the instrument's calibration curve. Element specific instrument conditions are listed in Section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annually and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for arsenic in aqueous samples are reported below:

Element	MDL (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)
Arsenic	2.5	2.5	100

1.4. INTERFERENCES

1.4.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample digestion. Laboratory control samples are used to verify that the digestion procedure was appropriate. A matrix modifier is added to the sample to minimize volatilization losses during the drying and ashing steps of the graphite furnace temperature program and to minimize matrix interferences.

1.4.2 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. Zeeman background correction may also help to reduce certain chemical interferences such as the positive interference attributed to high concentrations of aluminum. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of aqueous samples with a mixture of nitric acid and 30 percent hydrogen peroxide. Both of these reagents are corrosive, and adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain nitric acid, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;

2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;

2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;

2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);

2.1.5 Disposable beakers, 10-mL capacity;

2.1.6 Class A volumetric flasks (1000 mL, 200 mL, 100 mL);

2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);

2.1.8 Graduated cylinders (50 mL);

2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;

2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer instrument equipped with a Model HGA-600 graphite furnace, Zeeman background correction, an electrodeless discharge lamp (EDL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube with L'vov platform;

2.2.2 Purge gas - Argon, 99.9% pure;

2.2.3 Matrix modifier - 500 ppm palladium nitrate;

2.2.4 Sample injection volume - 20 uL;

2.2.5 Matrix modifier injection volume - 5 uL;

2.2.6 Duplicate burns for all standards and samples with the average reported as the final result;

2.2.7 Wavelength - 193.7 nanometers (nm);

2.2.8 Slitwidth - 0.7 nm.

2.2.9 Arsenic furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	2-10	20-60
	2	300-500	5-20	10-40
	3	2000-2400	0-5	3-10
	4	2500-2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	1100-1400	5-20	20-60
	3	2000-2400	0-5	3-10
	4	2500-2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).

Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.

Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.

Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.

Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.

2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.

2.3.3 Hydrogen Peroxide (H_2O_2) - 30 percent, trace metals grade.

2.3.4 Nitric acid (1+1) - using a 100 mL graduated cylinder, 100 mL of conc. HNO_3 is added to 100 mL deionized water and placed in a nalgene dispenser bottle.

2.3.5 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.6 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 As standard solution: Use a commercially purchased 1,000 milligram-per-liter (mg/L) stock solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Arsenic Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L arsenic stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 100 μg/L Arsenic Standard (C2): Using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L arsenic intermediate (C1) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 μg/L Arsenic Standard (C3): Using a volumetric pipet, 10 mL of the 100 μg/L arsenic standard (C2) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 100 μg/L and 10 μg/L arsenic standards with a 5% HNO_3 solution (see Sec. 3.1).

2.4.6 5 mg/L Arsenic Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L arsenic stock is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NIST reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 50 ug/L As continuing calibration verification solution (CCV): using a volumetric pipet transfer 1.0 mL of the 10 mg/L arsenic intermediate (C1) is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 5-percent HNO_3 solution: using a Nalgene dispenser bottle, 5 mL conc. HNO_3 is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for As is 7740-38-2, its atomic weight is 74.92 and density 5.73 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

100 ug/L and 10 ug/L arsenic standards are prepared as outlined in Sec. 2.4. Additional calibration standards for As are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Arsenic

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	100	20	0	100
C2	100	10	10	50
C2	100	5	15	25
C3	10	20	0	10
C3	10	5	15	2.5
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for As by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration, the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 100 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (50 ug/L As) is reanalyzed. If the measured concentration for this standard is not $\pm$ 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Aqueous samples for metals analysis must be preserved with nitric acid to a pH of less than 2. The pH of the sample should be checked after addition to the container to insure that the pH is less than or equal to 2, and more acid added if necessary.

4.2 SAMPLING CONTAINERS

Aqueous samples are taken in one liter polypropylene bottles with screw caps.

4.3 STORAGE CONDITIONS

Samples are shipped to and stored in the laboratory at room temperature.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 PROCEDURE

5.1. SAMPLE DIGESTION

5.1.1 Using a graduated cylinder, transfer a 50 mL aliquot of well-mixed sample to a 150 mL beaker. Add 1.0 mL of 30% H_2O_2 and 0.5 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place on a hot plate and heat at 95°C until digestion is complete or the volume is reduced to 20-25 mL. Do not allow the sample to boil.

5.1.2 Remove the beaker and allow to cool. Add 2.0 mL conc. HNO_3. Wash down the beaker walls with Type I water and filter, if necessary. Filtration should be done only if there is concern that insoluble material may clog the autosampler. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute HNO_3 prior to use.

5.1.3 Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 5% (v/v) HNO_3.

5.1.4 Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.5 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.6 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.7 Enter the digestion date in the computer.

5.1.8 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in Sec. 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7060 (1986).

5.2.5 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported arsenic concentration for that sample should be qualified as having a possible interference.

5.2.6 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.7 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.8 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within $\pm$ 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.9 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.10 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.11 When MSA is required, four 5.0 mL aliquots of sample are spiked with 0, 20, 40, and 60 uL respectively of a 5.0 mg/L As solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (cc) for each set. If the cc is less than 0.995, repeat the analysis once. If the cc is still less than 0.995, the original sample response will be reported and qualified as having a possible interference.

5.2.12 Attachment 3 shows a typical GFAA run sequence.

6.0 CALCULATIONS

6.1 The Perkin-Elmer 5100Z and 4100ZL instruments determine the absorbance-seconds of As in the sample digestate and calculate the sample concentration in ug/L directly from the standard curve. If the sample concentration of As is within the calibration range, the sample concentration will be reported as as calculated by the instrument. If the concentration of As is either not detected or below the method detection limit, the sample concentration will be reported as less than the method detection limit. If the concentration of As is greater than the highest calibration standard, the sample digestate should be diluted within range and reanalyzed. The concentration in the diluted sample and the dilution factor are reported. The highest calibration range for As is 100 ug/L as given in Sec. 1.3. When MSA is performed, the result from this analysis will be used unless the cc <0.995.

6.2 Post digestion spikes (SPX) are prepared by adding one part high standard (100 ug/L) to one part sample. A dilution factor of two is entered in the data batch and the target concentration will equal the concentration of the high standard (100 ug/L).

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, 0.5 mL of 1000 ppm stock standard that is purchased commercially is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 500 ug-As/L. This solution is prepared fresh monthly (see Section 2.4.10 for policy on stock standard source).

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 50 mL of deionized water:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)
Blank	--	0
Low	0.5	5.0
High	5.0	50.0
High	5.0	50.0

7.1.3 When required, sample matrix spikes are prepared by adding 5.0 mL of the spike solution to 2-50 mL aliquots of the sample. The target concentration will be 50 ug/L.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.

2. Difference between the two high concentration spiked QC samples in each lot.

3. Three-point moving average percent recovery for the low level spike in each lot.

4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.5 EPA Method 7060 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

October 27, 1993

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (As & Se)	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of As & Se 1000 ppm stock standards are transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for As & Se. This solution is prepared fresh monthly.

2. Prepare quality control samples:
   a. Method blank (MB) - reagents only.
   b. Low spike (SP1) - add 0.5 mL of spike solution to 50 mL DI.
   c. High spike (SP2, SP3)- add 5.0 mL of spike solution to 2-50 mL aliquots of DI.
   d. Sample matrix spikes (SPM1, SPM2)- add 5.0 mL of spike solution to 2-50 mL aliquots of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
As, Se	5 ug/L	50 ug/L	50 ug/L

DIGESTION PROCEDURE:

1. Using a graduated cylinder, transfer a 50 mL aliquot of well-mixed sample to a 150 mL beaker. Add 1.0 mL of 30% H_2O_2 and 0.5 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place on a hot plate and heat at 95°C until digestion is complete or the volume is reduced to 20-25 mL. Do not allow the sample to boil.

2. Remove the beaker and allow to cool. Add 2.0 mL conc. HNO_3. Wash down the beaker walls with Type I water and filter, if necessary. Filtration should be done only if there is concern that insoluble material may clog the autosampler. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute HNO_3 prior to use.

3. Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 5% (v/v) HNO_3.

4. Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

5. Enter the digestion date in the computer.

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (As & Se)	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.

2. Prepare the following standards for instrument dilution (Note: standards should be 5% HNO_3):

Element	Conc.(ug/L)	Calibration Curves (ug/L)
As, Se	100 & 10	100, 50, 25, 10, 2.5, 0.0

3. Method detection limits (MDL):
   As & Se = 2.5 ug/L

4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.

5. Analyze the standard curve. The cc must be > 0.995.

6. Analyze the ICV. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

7. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.

8. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD is greater than 20% for a sample whose concentration exceeds twice the MDL, reanalyze the sample. If RPD is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.

9. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

10. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

11. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not ± 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L MSA solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (As & Se)	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS (Chemical Laboratory Analysis and Scheduling System) data batch. CLASS is ESE's computerized data management system.

2. If the method blank has a response greater than the instrument detection limit the data must be reviewed by the department manager to determine is the data is acceptable.

3. If the method blank (or any sample with a SPM or SPX) has a response less than the instrument detection limit, enter the response as 0 Final so that CLASS will not use the response in the recovery calculations.

4. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.

5. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 - TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank		
Standard 1 (2.5 ug/L)		
Standard 2 (10.0 ug/L)		
Standard 3 (25.0 ug/L)		
Standard 4 (50.0 ug/L)		
Standard 5 (100 ug/L)		
Initial calibration verification - ICV (reference)		± 10%
Method blank (MB)		
Low spike (SP1)	see control charts	
High spike (SP2)	see control charts	
High spike (SP3)	see control charts	
Sample #1		
Sample #1 matrix spike		
Sample #1 matrix spike dup		
Sample #2		
CCV (50 ug/L)		± 10%
Continuing calibration blank - CCB		
Sample #3 through #12		
CCV (50 ug/L)		± 10%
CCB		
Sample #13 through #20		
Serial Dilution (1+4)		± 10%
or Post-Digestion Spike (SPX)		± 15%
CCV (50 ug/L)		± 10%
CCB		
MSA - 0		
MSA - 1		
MSA - 2		
MSA - 3		
CCV (50 ug/L)		± 10%
CCB		

ATTACHMENT 3.0 - MDL STUDY

October 27, 1993

GFAA Instrument & Method Detection Limits
JANUARY 1993

Element	Spike Conc. (ug/L)	Day 1 Response (ug/L)	Day 1 SD (ug/L)	Day 2 Response (ug/L)	Day 2 SD (ug/L)	Day 3 Response (ug/L)	Day 3 SD (ug/L)	IDL (ug/L)	Combined Reported IDL (ug/L)	Unspiked Response (ug/L)	Spiked Response (ug/L)	MDL (ug/L)	Combined Reported MDL (ug/L)
Arsenic	5.0	5.4	0.90	4.4	0.29	4.5	0.78	2.0	2.0	0.0	4.9	1.5	2.5
5100A		5.2		4.9		6.1					4.6		
		6.9		4.9		4.0					4.9		
		5.5		4.4		4.1					4.1		
		7.6		4.7		4.6					4.1		
		6.2		4.9		3.7					4.6		
		5.5		4.2		4.7					5.5		
5100B	5.0	5.0	0.55	3.9	0.52	5.4	0.38	1.4		0.4	6.0	1.0	
		4.2		4.3		5.5					5.3		
		5.5		4.2		5.0					5.4		
		4.3		4.9		4.9					5.3		
		5.3		4.4		5.7					5.0		
		4.3		3.3		6.0					5.3		
		5.2		3.7		5.3					5.4		
5100C	5.0	4.2	0.22	4.7	0.22	4.6	0.49	0.9		0.1	4.1	0.3	
		4.3		5.3		4.3					4.0		
		4.4		5.0		4.6					4.1		
		4.2		4.7		5.2					4.1		
		4.3		4.9		5.2					4.3		
		4.7		4.8		3.8					4.0		
		4.7		4.7		4.5					4.2		
4100	5.0	4.9	0.77	4.9	0.58	9.2	0.68	2.0		0.0	4.1	1.1	
		4.1		4.9		9.1					4.3		
		4.4		4.9		10.1					4.6		
		5.4		5.3		8.1					3.7		
		3.3		3.6		9.3					3.7		
		5.5		4.3		9.8					3.9		
		4.3		4.2		8.6					4.4		

Reference: CLP390 (ILM01.0) & 40 CFR 136, App. B/SW846

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **ANALYSIS OF SOIL AND SEDIMENT SAMPLES FOR ARSENIC BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY**
(SW-846 METHOD 3050/7060)
USAEC METHOD - GAS1 - SOIL

TABLE OF CONTENTS

TITLE: **ANALYSIS OF SOIL AND SEDIMENT SAMPLES FOR ARSENIC BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3050/7060) USAEC METHOD - GAS1 - SOIL**

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental soil and sediment samples for arsenic (As) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Soil and sediment samples for GFAAS determination are digested by EPA SW-846 Method 3050 and analyzed following EPA SW-846 Method 7060. The only deviation from these methods is the use of palladium nitrate as a matrix modifier instead of nickel nitrate based on the instrument manufacturer's recommendations.

1.2.2 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at twice the reporting limit and two spikes at twenty times the reporting limit will be digested and analyzed with each lot of samples.

1.2.3 A representative 1-2 g (wet weight) sample is prepared for analysis by refluxing on a hot plate at approximately 95°C with a mixture of nitric acid and hydrogen peroxide in a covered beaker. The digestate is then cooled, filtered and diluted to 100 mL.

1.2.4 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of

light at a specific wavelength during atomization is measured and the concentration of arsenic in the sample is calculated based on the instrument's calibration curve. Element specific instrument conditions are listed in section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annual and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for arsenic in soil and sediment samples are reported below:

Element	MDL (ug/g)	Lower Standard Range (ug/g)+	Upper Standard Range (ug/g)+
Arsenic	0.25	0.25	10.0

+ Based on 1 g of soil and 100 mL final volume

1.4. INTERFERENCES

1.4.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample digestion. Laboratory control samples are used to verify that the digestion procedure was appropriate. A matrix modifier is added to the sample to minimize volatilization losses during the drying and ashing steps of the graphite furnace temperature program and to minimize matrix interferences.

1.4.2 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. Zeeman background correction may also help to reduce certain chemical interferences such as the positive interference attributed to high concentrations of aluminum. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of soil and sediment samples with a mixture of nitric acid and 30 percent hydrogen peroxide. Both of these reagents are corrosive, and adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain nitric acid, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;

2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;

2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;

2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);

2.1.5 Disposable beakers, 10-mL capacity;

2.1.6 Class A volumetric flasks (1000 mL, 200 mL, 100 mL);

2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);

2.1.8 Graduated cylinders (100 mL);

2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;

2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer instrument equipped with a Model HGA-600 graphite furnace, Zeeman background correction, an electrodeless discharge lamp (EDL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube with L'vov platform;

2.2.2 Purge gas - Argon, 99.9% pure;

2.2.3 Matrix modifier - 500 ppm palladium nitrate;

2.2.4 Sample injection volume - 20 uL;

2.2.5 Matrix modifier injection volume - 5 uL;

2.2.6 Duplicate burns for all standards and samples with the average reported as the final result;

2.2.7 Wavelength - 193.7 nanometers (nm);

2.2.8 Slitwidth - 0.7 nm.

2.2.9 Arsenic furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	2-10	20-60
	2	300-500	5-20	10-40
	3	2000-2400	0-5	3-10
	4	2500-2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	1100-1400	5-20	20-60
	3	2000-2400	0-5	3-10
	4	2500-2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed

using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).

Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.

Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.

Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.

Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.

2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.

2.3.3 Hydrogen Peroxide (H_2O_2) - 30 percent, trace metals grade.

2.3.4 Nitric acid (1+1) - using a 100 mL graduated cylinder, 100 mL of conc. HNO_3 is added to 100 mL deionized water and placed in a nalgene dispenser bottle.

2.3.5 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.6 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.3.7 USAEC Standard Soil.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 As standard solution: Use a commercially purchased 1,000 milligram-per-liter (mg/L) stock solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Arsenic Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L arsenic stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 100 μg/L Arsenic Standard (C2): Using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L arsenic intermediate (C1) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 μg/L Arsenic Standard (C3): Using a volumetric pipet, 10 mL of the 100 μg/L arsenic standard (C2) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 100 μg/L and 10 μg/L arsenic standards with a 5% HNO_3 solution (see Sec. 3.1).

2.4.6 5 mg/L Arsenic Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L arsenic stock is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NIST reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 50 ug/L As continuing calibration verification solution (CCV): using a volumetric pipet transfer 1.0 mL of the 10 mg/L arsenic intermediate (C1) is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 5-percent HNO_3 solution: using a Nalgene dispenser bottle, 5 mL conc. HNO_3 is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for As is 7740-38-2, its atomic weight is 74.92 and density 5.73 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

100 ug/L and 10 ug/L arsenic standards are prepared as outlined in Sec. 2.4. Additional calibration standards for As are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Arsenic

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	100	20	0	100
C2	100	10	10	50
C2	100	5	15	25
C3	10	20	0	10
C3	10	5	15	2.5
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for As by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 100 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (50 ug/L As) is reanalyzed. If the measured concentration for this standard is not $\pm$ 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Soil and sediment samples for metals analysis must be maintained in a temperature-controlled room at 4 degrees Celsius (°C).

4.2 SAMPLING CONTAINERS

Environmental soil and sediment samples are collected in wide-mouth, amber-glass jars with teflon-lined lids.

4.3 STORAGE CONDITIONS

Samples are shipped and stored in the laboratory at 4° C.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 PROCEDURE

5.1. SAMPLE DIGESTION

5.1.1 Mix the sample thoroughly to achieve homogeneity. Weigh directly into a beaker or erlenmeyer flask, a 1 to 2 g aliquot of sample to the nearest 0.0001 g. For samples with low percent solids a larger sample size may be necessary.

5.1.2 Add 10 mL of 1+1 HNO_3 and mix the slurry. The sample is covered with a non-ribbed watch glass and refluxed on a hot plate at 95°C for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.

5.1.3 Allow the sample to cool and add 2 mL Type I water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool.

5.1.4 Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than a total 10 mL of 30% H_2O_2.

5.1.5 Cover the beaker with a ribbed watch glass and continue heating until the volume has been reduced to approximately 5 mL. Remove the beaker and allow the sample to cool. Wash down the beaker walls with Type I water and filter or centrifuge the sample to remove particulates that could clog the GFAA autosampler during analyses. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute nitric acid prior to use.

5.1.6 Adjust the final volume to 100 mL with Type I water. The digested sample will have an approximate acid concentration of 5% (v/v) HNO_3.

5.1.7 A reagent blank should also be carried through the entire digestion procedure.

5.1.8 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.9 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.10 Enter the digestion date and sample weights in the computer.

5.1.11 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the reagent blank. If the reagent blank is greater than twice the method detection limit, the samples must be redigested and the newly prepared samples analyzed or an adequate explanation provided as to why the original samples should be acceptable.

5.2.5 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7060 (1986).

5.2.6 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported arsenic concentration for that sample should be qualified as having a possible interference.

5.2.7 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.8 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.9 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within $\pm$ 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.10 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.11 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.12 When MSA is required, four 5.0 mL aliquots of sample are spiked with 0, 20, 40, and 60 uL respectively of a 5.0 mg/L As solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (cc) for each set. If the cc is less than 0.995, repeat the analysis once. If the cc is still less than 0.995, the original sample response will be reported and qualified as having a possible interference.

5.2.13 Attachment 3 shows a typical GFAA run sequence.

6.0 CALCULATIONS

6.1 The Perkin-Elmer 5100Z and 4100ZL instruments determine the absorbance-seconds of As in the sample digestate and calculate the sample concentration in ug/L directly from the standard curve. If the sample concentration of As is within the calibration range, the sample concentration will be reported as calculated from Sec.6.2. If the concentration of As is either not detected or below the method detection limit, the sample concentration will be reported as less than the method detection limit. If the concentration of As is greater than the highest calibration standard, the sample digestate should be diluted within range and reanalyzed. The concentration in the diluted sample and the dilution

factor are reported. The highest calibration range for As is 10.0 ug/g (100 ug/L) as given in Sec. 1.3. When MSA is performed, the result from this analysis will be used unless the cc <0.995.

6.2 For soils and sediments, the measured ug/L concentration or MSA value, digested sample weight and percent solids are entered in the data batch. If a dilution was required, the concentration in the diluted sample and the dilution factor are entered in the data batch. Dry weight results are based on the following calculation:

$$\text{Conc, dry (ug/g)} = \frac{\text{Conc. in digestate (ug/L)} \times \text{Digestate vol. (L)}}{\text{Wet weight of sample (g)} \times \text{\% solids}}$$

6.3 Post digestion spikes (SPX) are prepared by adding one part high standard (100 ug/L) to one part sample. A dilution factor of two is entered in the data batch and the target concentration will equal the concentration of the high standard (100 ug/L).

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, 0.5 mL of 1000 ppm stock standard that is commercially purchased is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 500 ug-As/L. This solution is prepared fresh monthly (see Section 2.4.10 for policy on stock standard source).

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 0.1 g of standard soil:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)	Conc. of Control Spike (ug/g)$^+$
Blank	--	0	0
Low	1.0	5.0	0.5
High	10.0	50.0	5.0
High	10.0	50.0	5.0

+Note: ug/g target concentrations for control spikes are based on 1.0 g. The actual weight of standard soil is multiplied by 10 per USAEC instructions.

7.1.3 When required, sample matrix spikes are prepared by adding 10.0 mL of the spike solution to 2-1.0 g portions of the sample. The target concentration will be 5.0 ug/g.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.
2. Difference between the two high concentration spiked QC samples in each lot.
3. Three-point moving average percent recovery for the low level spike in each lot.
4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 3050 - Test Methods for Evaluating Solid Wastes, EPA SW 846, 3rd Edition, September 1986.

8.5 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.6 EPA Method 7060 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of As, Se, & Tl 1000 ppm stock standards 0.8 mL of Pb 1000 ppm stock standard, and 1.0 mL of V 1000 ppm stock standard are transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for As, Se, & Tl, 800 ug/L for Pb and 1000 ug/L for V. This solution is prepared fresh monthly.
2. Prepare quality control samples:
   a. Reagent blank - reagents only.
   b. Method blank (MB) - 0.1 g portion of standard soil plus reagents.
   c. Low spike (SP1) - add 1.0 mL of spike solution to 0.1 g portion of standard soil.
   d. High spike (SP2,SP3)- add 10.0 mL of spike solution to 2-0.1 g portions of standard soil.
   e. Sample matrix spikes (SPM1, SPM2)- add 10.0 mL of spike solution to 2-1.0 g portions of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
As, Se, Tl	0.5 ug/g (5 ug/L)	5.0 ug/g (50 ug/L)	5.0 ug/g (50 ug/L)
Pb	0.8 ug/g (8 ug/L)	8.0 ug/g (80 ug/L)	8.0 ug/g (80 ug/L)
V	1.0 ug/g (10 ug/L)	10.0 ug/g (100 ug/L)	10.0 ug/g (100 ug/L)

Note: ug/g target concentrations for low and high spike are based on 1.0 g.

DIGESTION PROCEDURE:

1. Mix the sample thoroughly. Weigh into a beaker or erlenmeyer flask, a 1-2 g aliquot of sample to the nearest 0.0001 g. For samples with low % solids a larger sample size may be necessary.
2. Add 10 mL of 1+1 HNO_3 and mix. Cover with a non-ribbed watch glass and reflux on a hot plate at 95°C for 10-15 minutes without boiling. Cool the sample, and add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.
3. Allow the sample to cool. Add 2 mL Type I water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool. Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or the general appearance is unchanged. Do not add more than a total 10 mL of H_2O_2.
4. Cover with a ribbed watch glass and continue heating until the volume has been reduced to approx. 5 mL. Remove the beaker and allow to cool. Wash down the beaker walls with deionized water and filter if necessary. Adjust the final volume to 100 mL with Type II water. The digested sample will have an approximate acid concentration of 5% (v/v) HNO_3.
5. Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.
6. Enter the digestion date and sample weights in the computer.

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.
2. Prepare the following standards for instrument dilution (Note: standards should be 5% HNO_3):

Element	Conc.(ug/L)	Calibration Curves (ug/L)
As,Pb,Se,Tl	100 & 10	100, 50, 25, 10, 2.5, 0.0
V	200 & 10	200, 100, 50, 10, 5.0, 0.0

3. Method detection limits (MDL):
   As = 0.25 ug/g (2.5 ug/L)   Tl = 0.25 ug/g (2.5 ug/L)
   Pb = 0.50 ug/g (5.0 ug/L)   V = 0.75 ug/g (7.5 ug/L)
   Se = 0.25 ug/g (2.5 ug/L)
4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.
5. Analyze the standard curve. The cc must be > 0.995.
6. Analyze the ICV. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.
7. Analyze the reagent blank. If the reagent blank is greater than twice the MDL, redigest the samples or provide an adequate explanation as to why the samples should be acceptable.
8. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.
9. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, reanalyze the sample. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.
10. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.
11. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.
12. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L MSA solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS (Chemical Laboratory Analysis and Scheduling System) data batch. CLASS is ESE's computerized data management system.
2. If the method blank has a response greater than the instrument detection limit, blank correction should be applied to the daily control spikes only. If the MB (or any sample with a matrix spike) has a negative response or is less than the instrument detection limit, enter the response as 0 Final.
3. Use 10X the actual standard soil weight for the method blank and control spike calculations.
4. Digestate volumes (0.1 L), weights (g) and % moisture should be supplied by CLASS. Verify the entries are correct. Responses should be uploaded in ug/L. (% Moisture for standard soil = 0.05). Include the sample %moisture summary in the data batch.
5. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.
6. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 - TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank		
Standard 1 (2.5 ug/L)		
Standard 2 (10.0 ug/L)		
Standard 3 (25.0 ug/L)		
Standard 4 (50.0 ug/L)		
Standard 5 (100 ug/L)		
Initial calibration verification - ICV (reference)		± 10%
Reagent blank		
Method blank (MB)		
Low spike (SP1)	see control charts	
High spike (SP2)	see control charts	
High spike (SP3)	see control charts	
Sample #1		
Sample #1 matrix spike		
Sample #1 matrix spike dup		
Sample #2		
CCV (50 ug/L)		± 10%
Continuing calibration blank - CCB		
Sample #3 through #12		
CCV (50 ug/L)		± 10%
CCB		
Sample #13 through #20		
Serial Dilution (1+4)		± 10%
or Post-Digestion Spike (SPX)		± 15%
CCV (50 ug/L)		± 10%
CCB		
MSA - 0		
MSA - 1		
MSA - 2		
MSA - 3		
CCV (50 ug/L)		± 10%
CCB		

ATTACHMENT 3.0 - MDL STUDY

October 27, 1993

GFAA Soil/Sediment MDL Study
January 1993

Element	Spike Conc. (ug/L)	Spike Conc. (ug/g)	ERA-Unspiked Response (ug/g)	ERA-Spike Response (ug/L)	ERA-Spike Weight (g)	ERA-Spike Response (ug/g)	Standard Deviation (ug/g)	ERA Soil MDL (ug/g)	AEC-Unspiked Response (ug/g)	AEC-Spike Response (ug/L)	AEC-Spike Weight (g)x10	AEC-Spike Response (ug/g)	Standard Deviation (ug/g)	AEC Soil MDL (ug/g)	Combined Reported MDL (ug/g)
Arsenic	5.0	0.50	-0.0587	4.5	1.0128	0.4443	0.0413	0.130	0.1192	9.2	1.165	0.7897	0.056	0.18	0.25
5100A				4.5	1.0093	0.4459				8.3	1.017	0.8161			
				4.4	1.0064	0.4372				8.0	1.009	0.7929			
				5.6	1.0225	0.5477				7.0	1.064	0.6579			
				4.6	1.0194	0.4512				7.7	1.093	0.7045			
				4.8	1.0079	0.4762				7.8	1.014	0.7692			
				4.3	1.0124	0.4247				8.0	1.027	0.7790			
5100B	5.0	0.50	0.0000	6.0	1.0128	0.5924	0.0195	0.061	0.2016	8.8	1.165	0.7554	0.041	0.13	
				6.1	1.0093	0.6044				7.8	1.017	0.7670			
				5.7	1.0064	0.5664				8.4	1.009	0.8325			
				6.1	1.0225	0.5966				7.5	1.064	0.7049			
				5.9	1.0194	0.5788				7.9	1.093	0.7228			
				6.2	1.0079	0.6151				7.8	1.014	0.7692			
				5.7	1.0124	0.5630				7.7	1.027	0.7498			
5100C	5.0	0.50	0.0391	4.6	1.0128	0.4542	0.0118	0.037	0.0825	8.5	1.165	0.7296	0.043	0.14	
				4.9	1.0093	0.4855				7.9	1.017	0.7768			
				4.7	1.0064	0.4670				7.9	1.009	0.7830			
				4.7	1.0225	0.4597				7.5	1.064	0.7049			
				4.6	1.0194	0.4512				7.8	1.093	0.7136			
				4.7	1.0079	0.4663				8.3	1.014	0.8185			
				4.6	1.0124	0.4544				8.1	1.027	0.7887			
4100	5.0	0.50	0.0489	4.8	1.0128	0.4739	0.0383	0.121	0.1192	7.1	1.165	0.6094	0.055	0.17	
				5.0	1.0093	0.4954				7.0	1.017	0.6883			
				4.2	1.0064	0.4173				5.9	1.009	0.5847			
				4.0	1.0225	0.3912				6.4	1.064	0.6015			
				4.7	1.0194	0.4611				6.0	1.093	0.5489			
				4.9	1.0079	0.4862				7.0	1.014	0.6903			
				4.8	1.0124	0.4741				6.8	1.027	0.6621			

Reference: 40 CFR 136, Appendix B (ERA Inorganic Blank Sand & AEC Standard Soil)/SW846

GMDLSOIL

SELENIUM BY GFAA
(USAEC METHOD GSE1)

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **ANALYSIS OF AQUEOUS SAMPLES FOR SELENIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY**
(SW-846 METHOD 3020/7740)
USAEC METHOD - GSE1 - WATER

TABLE OF CONTENTS

TITLE: **ANALYSIS OF AQUEOUS SAMPLES FOR SELENIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7740) USAEC METHOD - GSE1 - WATER**

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental aqueous samples and wastes with suspended solids for selenium (Se) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Aqueous samples for GFAAS determination are digested by and analyzed following EPA SW-846 Method 7740.

1.2.2 There are three deviations from the SW-846 method: a) the initial and final volume of sample digested is 50 mL instead of 100 mL, b) after digestion, the acid concentration of the samples is adjusted to 5% to match soil samples prepared by SW-846 Method 3050 and aqueous samples prepared by SW-846 Method 3020 which allows the use of a single set of standards for all preps, and c) the use of palladium nitrate as a matrix modifier instead of nickel nitrate based on the instrument manufacturer's recommendations.

1.2.3 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at twice the reporting limit and two spikes at twenty times the reporting limit will be digested and analyzed with each lot of samples.

1.2.4 A representative 50 mL aliquot of sample is prepared for analysis by refluxing on a hot plate at approximately 95°C with a mixture of nitric acid and hydrogen peroxide in a covered beaker. The digestate is then cooled, filtered and diluted to 50 mL.

1.2.5 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of light at a specific wavelength during atomization is measured and the concentration of selenium in the sample is calculated based on the instrument's calibration curve. Element specific instrument conditions are listed in section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annual and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for selenium in aqueous samples are reported below:

Element	MDL (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)
Selenium	2.5	2.5	100

1.4. INTERFERENCES

1.4.1 Elemental selenium and many of its compounds are volatile; therefore, samples may be subject to losses of selenium during sample digestion. Laboratory control samples are used to verify that the digestion procedure was appropriate. A matrix modifier is added to the sample to minimize volatilization losses during the drying and ashing steps of the graphite furnace temperature program and to minimize matrix interferences.

1.4.2 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. Zeeman background correction may also help to reduce certain chemical interferences such as the positive interference attributed to high concentrations of iron. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of aqueous samples with a mixture of nitric acid and 30 percent hydrogen peroxide. Both of these reagents are corrosive, and adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain nitric acid, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;

2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;

2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;

2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);

2.1.5 Disposable beakers, 10-mL capacity;

2.1.6 Class A volumetric flasks (1000 mL, 200 mL, 100 mL);

2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);

2.1.8 Graduated cylinders (50 mL);

2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;

2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer instrument equipped with a Model HGA-600 graphite furnace, Zeeman background correction, an electrodeless discharge lamp (EDL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube with L'vov platform;

2.2.2 Purge gas - Argon, 99.9% pure;

2.2.3 Matrix modifier - 500 ppm palladium nitrate;

2.2.4 Sample injection volume - 20 uL;

2.2.5 Matrix modifier injection volume - 5 uL;

2.2.6 Duplicate burns for all standards and samples with the average reported as the final result;

2.2.7 Wavelength - 196.0 nanometers (nm);

2.2.8 Slitwidth - 0.7 nm.

2.2.9 Selenium furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	2-10	20-60
	2	300-500	2-20	10-40
	3	2000-2200	0-5	3-10
	4	2400-2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	900-1200	5-20	20-60
	3	2000-2200	0-5	3-10
	4	2500-2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).

Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.

Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.

Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.

Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.

2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.

2.3.3 Hydrogen Peroxide (H_2O_2) - 30 percent, trace metals grade.

2.3.4 Nitric acid (1+1) - using a 100 mL graduated cylinder, 100 mL of conc. HNO_3 is added to 100 mL deionized water and placed in a nalgene dispenser bottle.

2.3.5 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.6 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 Se standard solution: Use a commercially purchased 1,000 milligram-per-liter (mg/L) stock solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Selenium Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L selenium stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 100 μg/L Selenium Standard (C2): Using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L selenium intermediate (C1) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 μg/L Selenium Standard (C3): Using a volumetric pipet, 10 mL of the 100 μg/L selenium standard (C2) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 100 μg/L and 10 μg/L selenium standards with a 5% HNO_3 solution (see Sec. 3.1).

2.4.6 5 mg/L Selenium Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L selenium stock is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NIST reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 50 ug/L Se continuing calibration verification solution (CCV): using a volumetric pipet transfer 1.0 mL of the 10 mg/L selenium intermediate (C1) is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 5-percent HNO_3 solution: using a Nalgene dispenser bottle, 5 mL conc. HNO_3 is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for Se is 7782-49-2, its atomic weight is 78.96 and density 4.81 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

100 ug/L and 10 ug/L selenium standards are prepared as outlined in Sec. 2.4. Additional calibration standards for Se are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Selenium

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	100	20	0	100
C2	100	10	10	50
C2	100	5	15	25
C3	10	20	0	10
C3	10	5	15	2.5
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for Se by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 100 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (50 ug/L Se) is reanalyzed. If the measured concentration for this standard is not ± 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Aqueous samples for metals analysis must be preserved with nitric acid to a pH of less than 2. The pH of the sample should be checked after addition to the container to insure that the pH is less than or equal to 2, and more acid added if necessary.

4.2 SAMPLING CONTAINERS

Aqueous samples are taken in one liter polypropylene bottles with screw caps.

4.3 STORAGE CONDITIONS

Samples are shipped to and stored in the laboratory at room temperature.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 PROCEDURE

5.1. SAMPLE DIGESTION

5.1.1 Using a graduated cylinder, transfer a 50 mL aliquot of well-mixed sample to a 150 mL beaker. Add 1.0 mL of 30% H_2O_2 and 0.5 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place on a hot plate and heat at 95°C until digestion is complete or the volume is reduced to 20-25 mL. Do not allow the sample to boil.

5.1.2 Remove the beaker and allow to cool. Add 2.0 mL conc. HNO_3. Wash down the beaker walls with Type I water and filter, if necessary. Filtration should be done only if there is concern that insoluble material may clog the autosampler. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute HNO_3 prior to use.

5.1.3 Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 5% (v/v) HNO_3.

5.1.4 Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.5 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.6 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.7 Enter the digestion date in the computer.

5.1.8 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7740 (1986).

5.2.5 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported selenium concentration for that sample should be qualified as having a possible interference.

5.2.6 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.7 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.8 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.9 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.10 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.11 When MSA is required, four 5.0 mL aliquots of sample are spiked with 0, 20, 40, and 60 uL respectively of a 5.0 mg/L Se solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (cc) for each set. If the cc is less than 0.995, repeat the analysis once. If the cc is still less than 0.995, the original sample response will be reported and qualified as having a possible interference.

5.2.12 Attachment 3 shows a typical GFAA run sequence.

6.0 CALCULATIONS

6.1 The Perkin-Elmer 5100Z and 4100ZL instruments determine the absorbance-seconds of Se in the sample digestate and calculate the sample concentration in ug/L directly from the standard curve. If the sample concentration of Se is within the calibration range, the sample concentration will be reported as as calculated by the instrument. If the concentration of Se is either not detected or below the method detection limit, the sample concentration will be reported as less than the method detection limit. If the concentration of Se is greater than the highest calibration standard, the sample digestate should be diluted within range and reanalyzed. The concentration in the diluted sample and the dilution factor are reported. The highest calibration range for Se is 100 ug/L as given in Sec. 1.3. When MSA is performed, the result from this analysis will be used unless the cc <0.995.

6.2 Post digestion spikes (SPX) are prepared by adding one part high standard (100 ug/L) to one part sample. A dilution factor of two is entered in the data batch and the target concentration will equal the concentration of the high standard (100 ug/L).

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, 0.5 mL of 1000 ppm stock standard that is purchased commercially is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 500 ug-Se/L. This solution is prepared fresh monthly (see Section 2.4.10 for policy on stock standard source).

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 50 mL of deionized water:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)
Blank	--	0
Low	0.5	5.0
High	5.0	50.0
High	5.0	50.0

7.1.3 When required, sample matrix spikes are prepared by adding 5.0 mL of the spike solution to 2-50 mL aliquots of the sample. The target concentration will be 50 ug/L.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.

2. Difference between the two high concentration spiked QC samples in each lot.

3. Three-point moving average percent recovery for the low level spike in each lot.

4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.5 EPA Method 7740 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

October 27, 1993

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (As & Se)	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of As & Se 1000 ppm stock standards are transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for As & Se. This solution is prepared fresh monthly.

2. Prepare quality control samples:
   a. Method blank (MB) - reagents only.
   b. Low spike (SP1) - add 0.5 mL of spike solution to 50 mL DI.
   c. High spike (SP2, SP3)- add 5.0 mL of spike solution to 2-50 mL aliquots of DI.
   d. Sample matrix spikes (SPM1, SPM2)- add 5.0 mL of spike solution to 2-50 mL aliquots of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
As, Se	5 ug/L	50 ug/L	50 ug/L

DIGESTION PROCEDURE:

1. Using a graduated cylinder, transfer a 50 mL aliquot of well-mixed sample to a 150 mL beaker. Add 1.0 mL of 30% H_2O_2 and 0.5 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place on a hot plate and heat at 95°C until digestion is complete or the volume is reduced to 20-25 mL. Do not allow the sample to boil.

2. Remove the beaker and allow to cool. Add 2.0 mL conc. HNO_3. Wash down the beaker walls with Type I water and filter, if necessary. Filtration should be done only if there is concern that insoluble material may clog the autosampler. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute HNO_3 prior to use.

3. Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 5% (v/v) HNO_3.

4. Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

5. Enter the digestion date in the computer.

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (As & Se)	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.

2. Prepare the following standards for instrument dilution (Note: standards should be 5% HNO_3):

Element	Conc.(ug/L)	Calibration Curves (ug/L)
As, Se	100 & 10	100, 50, 25, 10, 2.5, 0.0

3. Method detection limits (MDL):
   As & Se = 2.5 ug/L

4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.

5. Analyze the standard curve. The cc must be > 0.995.

6. Analyze the ICV. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

7. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.

8. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD is greater than 20% for a sample whose concentration exceeds twice the MDL, reanalyze the sample. If RPD is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.

9. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

10. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

11. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not ± 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L MSA solution. Analyze each spike, and calculate the slope, x-

intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (As & Se)	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS (Chemical Laboratory Analysis and Scheduling System) data batch. CLASS is ESE's computerized data management system.

2. If the method blank has a response greater than the instrument detection limit the data must be reviewed by the department manager to determine is the data is acceptable.

3. If the method blank (or any sample with a SPM or SPX) has a response less than the instrument detection limit, enter the response as 0 Final so that CLASS will not use the response in the recovery calculations.

4. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.

5. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 -TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank	
Standard 1 (2.5 ug/L)	
Standard 2 (10.0 ug/L)	
Standard 3 (25.0 ug/L)	
Standard 4 (50.0 ug/L)	
Standard 5 (100 ug/L)	
Initial calibration verification - ICV (reference)	± 10%
Method blank (MB)	
Low spike (SP1)	see control charts
High spike (SP2)	see control charts
High spike (SP3)	see control charts
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike dup	
Sample #2	
CCV (50 ug/L)	± 10%
Continuing calibration blank - CCB	
Sample #3 through #12	
CCV (50 ug/L)	± 10%
CCB	
Sample #13 through #20	
Serial Dilution (1+4)	± 10%
or Post-Digestion Spike (SPX)	± 15%
CCV (50 ug/L)	± 10%
CCB	
MSA - 0	
MSA - 1	
MSA - 2	
MSA - 3	
CCV (50 ug/L)	± 10%.
CCB	

ATTACHMENT 3.0 - METHOD DETECTION LIMIT STUDIES

GFAA Instrument & Method Detection Limits
JANUARY 1993

Element	Spike Conc. (ug/L)	Day 1 Response (ug/L)	Day 1 SD (ug/L)	Day 2 Response (ug/L)	Day 2 SD (ug/L)	Day 3 Response (ug/L)	Day 3 SD (ug/L)	IDL (ug/L)	Combined Reported IDL (ug/L)	Unspiked Response (ug/L)	Spiked Response (ug/L)	MDL (ug/L)	Combined Reported MDL (ug/L)
Selenium	5.0	5.2	0.74	3.8	0.98	5.6	0.69	2.4	2.5	0.8	4.7	1.4	2.5
5100A		5.0		4.0		5.0					5.0		
		4.0		3.9		3.8					5.0		
		6.5		6.2		5.4					5.3		
		5.0		5.2		5.1					4.8		
		5.3		5.3		4.2					5.8		
		5.5		5.8		4.2					4.4		
5100B	5.0	5.5	0.53	5.6	0.66	5.9	0.58	1.8		0.6	4.7	0.8	
		5.6		4.4		5.0					4.8		
		4.8		4.5		5.0					4.4		
		4.7		5.9		6.4					4.7		
		4.7		4.7		5.2					4.2		
		4.3		5.9		6.2					5.0		
		5.6		4.8		5.4					4.8		
5100C	5.0	5.0	0.34	5.5	0.55	5.1	0.44	1.3		0.0	4.7	1.0	
		4.6		5.2		5.2					4.3		
		4.9		4.7		5.6					4.7		
		4.7		4.0		5.3					4.1		
		4.3		5.0		5.0					5.1		
		4.3		4.3		4.2					4.5		
		4.1		5.3		5.3					4.6		
4100	5.0	3.8	0.79	5.3	0.73	4.1	0.47	2.0		0.0	3.7	0.8	
		3.0		5.6		4.1					4.3		
		4.1		4.2		3.2					3.8		
		5.0		5.1		3.0					3.7		
		2.6		6.2		4.0					3.8		
		3.9		4.9		3.2					4.1		
		4.1		4.2		3.6					3.6		

Reference: CLP390 (ILM01.0) & 40 CFR 136, App. B/SW846

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Gainesville, Florida

TITLE: **ANALYSIS OF SOIL AND SEDIMENT SAMPLES FOR SELENIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3050/7740)**
USAEC METHOD - GSE1 -SOIL

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TITLE: **ANALYSIS OF SOIL AND SEDIMENT SAMPLES FOR SELENIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3050/7740)**
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1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental soil and sediment samples for selenium (Se) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Soil and sediment samples for GFAAS determination are digested by EPA SW-846 Method 3050 and analyzed following EPA SW-846 Method 7740. The only deviation from these methods is the use of palladium nitrate as a matrix modifier instead of nickel nitrate based on the instrument manufacturer's recommendations.

1.2.2 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at twice the reporting limit and two spikes at twenty times the reporting limit will be digested and analyzed with each lot of samples.

1.2.3 A representative 1-2 g (wet weight) sample is prepared for analysis by refluxing on a hot plate at approximately 95°C with a mixture of nitric acid and hydrogen peroxide in a covered beaker. The digestate is then cooled, filtered and diluted to 100 mL.

1.2.4 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of light at a specific wavelength during atomization is measured and the

concentration of selenium in the sample is calculated based on the instrument's calibration curve. Element specific instrument conditions are listed in section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annual and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for selenium in soil and sediment samples are reported below:

Element	MDL (ug/g)	Lower Standard Range (ug/g)+	Upper Standard Range (ug/g)+
Selenium	0.25	0.25	10.0

+ Based on 1 g of soil and 100 mL final volume

1.4. INTERFERENCES

1.4.1 Elemental selenium and many of its compounds are volatile; therefore, samples may be subject to losses of selenium during sample digestion. Laboratory control samples are used to verify that the digestion procedure was appropriate. A matrix modifier is added to the sample to minimize volatilization losses during the drying and ashing steps of the graphite furnace temperature program and to minimize matrix interferences.

1.4.2 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. Zeeman background correction may also help to reduce certain chemical interferences such as the positive interference attributed to high concentrations of iron. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of soil and sediment samples with a mixture of nitric acid and 30 percent hydrogen peroxide. Both of these reagents are corrosive, and adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain nitric acid, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;

2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;

2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;

2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);

2.1.5 Disposable beakers, 10-mL capacity;

2.1.6 Class A volumetric flasks (1000 mL, 200 mL, 100 mL);

2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);

2.1.8 Graduated cylinders (100 mL);

2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;

2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer instrument equipped with a Model HGA-600 graphite furnace, Zeeman background correction, an electrodeless discharge lamp (EDL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube with L'vov platform;

2.2.2 Purge gas - Argon, 99.9% pure;

2.2.3 Matrix modifier - 500 ppm palladium nitrate;

2.2.4 Sample injection volume - 20 uL;

2.2.5 Matrix modifier injection volume - 5 uL;

2.2.6 Duplicate burns for all standards and samples with the average reported as the final result;

2.2.7 Wavelength - 196.0 nanometers (nm);

2.2.8 Slitwidth - 0.7 nm.

2.2.9 Selenium furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	2-10	20-60
	2	300-500	2-20	10-40
	3	2000-2200	0-5	3-10
	4	2400-2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	900-1200	5-20	20-60
	3	2000-2200	0-5	3-10
	4	2500-2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed

using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).

Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.

Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.

Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.

Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.

2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.

2.3.3 Hydrogen Peroxide (H_2O_2) - 30 percent, trace metals grade.

2.3.4 Nitric acid (1+1) - using a 100 mL graduated cylinder, 100 mL of conc. HNO_3 is added to 100 mL deionized water and placed in a nalgene dispenser bottle.

2.3.5 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.6 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.3.7 USAEC Standard Soil.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 Se standard solution: Use a commercially purchased 1,000 milligram-per-liter (mg/L) stock solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Selenium Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L selenium stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 100 μg/L Selenium Standard (C2): Using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L selenium intermediate (C1) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 μg/L Selenium Standard (C3): Using a volumetric pipet, 10 mL of the 100 μg/L selenium standard (C2) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 100 μg/L and 10 μg/L selenium standards with a 5% HNO_3 solution (see Sec. 3.1).

2.4.6 5 mg/L Selenium Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L selenium stock is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NIST reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 50 ug/L Se continuing calibration verification solution (CCV): using a volumetric pipet transfer 1.0 mL of the 10 mg/L selenium intermediate (C1) is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 5-percent HNO_3 solution: using a Nalgene dispenser bottle, 5 mL conc. HNO_3 is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for Se is 7782-49-2, its atomic weight is 78.96 and density 4.81 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

100 ug/L and 10 ug/L selenium standards are prepared as outlined in Sec. 2.4. Additional calibration standards for Se are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Selenium

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	100	20	0	100
C2	100	10	10	50
C2	100	5	15	25
C3	10	20	0	10
C3	10	5	15	2.5
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for Se by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 100 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (50 ug/L Se) is reanalyzed. If the measured concentration for this standard is not $\pm$ 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Soil and sediment samples for metals analysis must be maintained in a temperature-controlled room at 4 degrees Celsius (°C).

4.2 SAMPLING CONTAINERS

Environmental soil and sediment samples are collected in wide-mouth, amber-glass jars with teflon-lined lids.

4.3 STORAGE CONDITIONS

Samples are shipped and stored in the laboratory at 4° C.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 PROCEDURE

5.1. SAMPLE DIGESTION

5.1.1 Mix the sample thoroughly to achieve homogeneity. Weigh directly into a beaker or erlenmeyer flask, a 1 to 2 g aliquot of sample to the nearest 0.0001 g. For samples with low percent solids a larger sample size may be necessary.

5.1.2 Add 10 mL of 1+1 HNO_3 and mix the slurry. The sample is covered with a non-ribbed watch glass and refluxed on a hot plate at 95°C for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.

5.1.3 Allow the sample to cool and add 2 mL Type I water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool.

5.1.4 Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than a total 10 mL of 30% H_2O_2.

5.1.5 Cover the beaker with a ribbed watch glass and continue heating until the volume has been reduced to approximately 5 mL. Remove the beaker and allow the sample to cool. Wash down the beaker walls with Type I water and filter or centrifuge the sample to remove particulates that could clog the GFAA autosampler during analyses. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute nitric acid prior to use.

5.1.6 Adjust the final volume to 100 mL with Type I water. The digested sample will have an approximate acid concentration of 5% (v/v) HNO_3.

5.1.7 A reagent blank should also be carried through the entire digestion procedure.

5.1.8 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.9 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.10 Enter the digestion date and sample weights in the computer.

5.1.11 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the reagent blank. If the reagent blank is greater than twice the method detection limit, the samples must be redigested and the newly prepared samples analyzed or an adequate explanation provided as to why the original samples should be acceptable.

5.2.5 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7740 (1986).

5.2.6 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported selenium concentration for that sample should be qualified as having a possible interference.

5.2.7 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.8 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.9 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within $\pm$ 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.10 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.11 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.12 When MSA is required, four 5.0 mL aliquots of sample are spiked with 0, 20, 40, and 60 uL respectively of a 5.0 mg/L Se solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (cc) for each set. If the cc is less than 0.995, repeat the analysis once. If the cc is still less than 0.995, the original sample response will be reported and qualified as having a possible interference.

5.2.13 Attachment 3 shows a typical GFAA run sequence.

6.0 CALCULATIONS

6.1 The Perkin-Elmer 5100Z and 4100ZL instruments determine the absorbance-seconds of Se in the sample digestate and calculate the sample concentration in ug/L directly from the standard curve. If the sample concentration of Se is within the calibration range, the sample concentration will be reported as calculated from Sec.6.2. If the concentration of Se is either not detected or below the method detection limit, the sample concentration will be reported as less than the method detection limit. If the concentration of Se is greater than the highest calibration standard, the sample digestate should be diluted within range and reanalyzed. The concentration in the diluted sample and the dilution

factor are reported. The highest calibration range for Se is 10.0 ug/g (100 ug/L) as given in Sec. 1.3. When MSA is performed, the result from this analysis will be used unless the cc <0.995.

6.2 For soils and sediments, the measured ug/L concentration or MSA value, digested sample weight and percent solids are entered in the data batch. If a dilution was required, the concentration in the diluted sample and the dilution factor are entered in the data batch. Dry weight results are based on the following calculation:

$$\text{Conc, dry (ug/g)} = \frac{\text{Conc. in digestate (ug/L) x Digestate vol. (L)}}{\text{Wet weight of sample (g) x \% solids}}$$

6.3 Post digestion spikes (SPX) are prepared by adding one part high standard (100 ug/L) to one part sample. A dilution factor of two is entered in the data batch and the target concentration will equal the concentration of the high standard (100 ug/L).

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, 0.5 mL of 1000 ppm stock standard that is commercially purchased is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 500 ug-Se/L. This solution is prepared fresh monthly (see Section 2.4.10 for policy on stock standard source).

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 0.1 g of standard soil:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)	Conc. of Control Spike (ug/g)$^{+}$
Blank	--	0	0
Low	1.0	5.0	0.5
High	10.0	50.0	5.0
High	10.0	50.0	5.0

+Note: ug/g target concentrations for control spikes are based on 1.0 g. The actual weight of standard soil used is multiplied by 10 per USAEC instructions.

7.1.3 When required, sample matrix spikes are prepared by adding 10.0 mL of the spike solution to 2-1.0 g portions of the sample. The target concentration will be 5.0 ug/g.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.
2. Difference between the two high concentration spiked QC samples in each lot.
3. Three-point moving average percent recovery for the low level spike in each lot.
4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 3050 - Test Methods for Evaluating Solid Wastes, EPA SW 846, 3rd Edition, September 1986.

8.5 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.6 EPA Method 7740 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of As, Se, & Tl 1000 ppm stock standards 0.8 mL of Pb 1000 ppm stock standard, and 1.0 mL of V 1000 ppm stock standard are transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for As, Se, & Tl, 800 ug/L for Pb and 1000 ug/L for V. This solution is prepared fresh monthly.
2. Prepare quality control samples:
   a. Reagent blank - reagents only.
   b. Method blank (MB) - 0.1 g portion of standard soil plus reagents.
   c. Low spike (SP1) - add 1.0 mL of spike solution to 0.1 g portion of standard soil.
   d. High spike (SP2,SP3)- add 10.0 mL of spike solution to 2-0.1 g portions of standard soil.
   e. Sample matrix spikes (SPM1, SPM2)- add 10.0 mL of spike solution to 2-1.0 g portions of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
As, Se, Tl	0.5 ug/g (5 ug/L)	5.0 ug/g (50 ug/L)	5.0 ug/g (50 ug/L)
Pb	0.8 ug/g (8 ug/L)	8.0 ug/g (80 ug/L)	8.0 ug/g (80 ug/L)
V	1.0 ug/g (10 ug/L)	10.0 ug/g (100 ug/L)	10.0 ug/g (100 ug/L)

Note: ug/g target concentrations for low and high spike are based on 1.0 g.

DIGESTION PROCEDURE:

1. Mix the sample thoroughly. Weigh into a beaker or erlenmeyer flask, a 1-2 g aliquot of sample to the nearest 0.0001 g. For samples with low % solids a larger sample size may be necessary.
2. Add 10 mL of 1+1 HNO_3 and mix. Cover with a non-ribbed watch glass and reflux on a hot plate at 95°C for 10-15 minutes without boiling. Cool the sample, and add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.
3. Allow the sample to cool. Add 2 mL Type I water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool. Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or the general appearance is unchanged. Do not add more than a total 10 mL of H_2O_2.
4. Cover with a ribbed watch glass and continue heating until the volume has been reduced to approx. 5 mL. Remove the beaker and allow to cool. Wash down the beaker walls with deionized water and filter if necessary. Adjust the final volume to 100 mL with Type II water. The digested sample will have an approximate acid concentration of 5% (v/v) HNO_3.
5. Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.
6. Enter the digestion date and sample weights in the computer.

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.
2. Prepare the following standards for instrument dilution (Note: standards should be 5% HNO_3):

Element	Conc.(ug/L)	Calibration Curves (ug/L)
As,Pb,Se,Tl	100 & 10	100, 50, 25, 10, 2.5, 0.0
V	200 & 10	200, 100, 50, 10, 5.0, 0.0

3. Method detection limits (MDL):
   As = 0.25 ug/g (2.5 ug/L) Tl = 0.25 ug/g (2.5 ug/L)
   Pb = 0.50 ug/g (5.0 ug/L) V = 0.75 ug/g (7.5 ug/L)
   Se = 0.25 ug/g (2.5 ug/L)
4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.
5. Analyze the standard curve. The cc must be > 0.995.
6. Analyze the ICV. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.
7. Analyze the reagent blank. If the reagent blank is greater than twice the MDL, redigest the samples or provide an adequate explanation as to why the samples should be acceptable.
8. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.
9. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, reanalyze the sample. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.
10. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.
11. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.
12. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L MSA solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS (Chemical Laboratory Analysis and Scheduling System) data batch. CLASS is ESE's computerized data management system.
2. If the method blank has a response greater than the instrument detection limit, blank correction should be applied to the daily control spikes only. If the MB (or any sample with a matrix spike) has a negative response or is less than the instrument detection limit, enter the response as 0 Final.
3. Use 10X the actual standard soil weight for the method blank and control spike calculations.
4. Digestate volumes (0.1 L), weights (g) and % moisture should be supplied by CLASS. Verify the entries are correct. Responses should be uploaded in ug/L. (% Moisture for standard soil = 0.05). Include the sample %moisture summary in the data batch.
5. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.
6. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 - TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank	
Standard 1 (2.5 ug/L)	
Standard 2 (10.0 ug/L)	
Standard 3 (25.0 ug/L)	
Standard 4 (50.0 ug/L)	
Standard 5 (100 ug/L)	
Initial calibration verification - ICV (reference)	± 10%
Reagent blank	
Method blank (MB)	
Low spike (SP1)	see control charts
High spike (SP2)	see control charts
High spike (SP3)	see control charts
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike dup	
Sample #2	
CCV (50 ug/L)	± 10%
Continuing calibration blank - CCB	
Sample #3 through #12	
CCV (50 ug/L)	± 10%
CCB	
Sample #13 through #20	
Serial Dilution (1+4)	± 10%
or Post-Digestion Spike (SPX)	± 15%
CCV (50 ug/L)	± 10%
CCB	
MSA - 0	
MSA - 1	
MSA - 2	
MSA - 3	
CCV (50 ug/L)	± 10%
CCB	

ATTACHMENT 3.0 - MDL STUDY

October 27, 1993

GFAA Soil/Sediment MDL Study
January 1993

Element	Spike Conc. (ug/L)	Spike Conc. (ug/g)	ERA-Unspiked Response (ug/g)	ERA-Spike Response (ug/L)	ERA-Spike Weight (g)	ERA-Spike Response (ug/g)	Standard Deviation (ug/g)	ERA Soil MDL (ug/g)	AEC-Unspiked Response (ug/g)	AEC-Spike Response (ug/L)	AEC-Spike Weight (g)x10	AEC-Spike Response (ug/g)	Standard Deviation (ug/g)	AEC Soil MDL (ug/g)	Combined Reported MDL (ug/~~L~~ g)
Selenium 5100A	5.0	0.05	0.0489	5.3	1.0128	0.5233	0.0433	0.136	0.0917	4.9	1.165	0.4206	0.035	0.11	0.25
				4.1	1.0093	0.4062				4.7	1.017	0.4621			
				4.5	1.0064	0.4471				3.6	1.009	0.3568			
				4.5	1.0225	0.4401				4.0	1.064	0.3759			
				5.2	1.0194	0.5101				4.7	1.093	0.4300			
				4.9	1.0079	0.4862				4.1	1.014	0.4043			
				5.1	1.0124	0.5038				4.0	1.027	0.3895			
5100B	5.0	0.05	0.0000	4.9	1.0128	0.4838	0.0383	0.120	0.0000	4.1	1.165	0.3519	0.039	0.12	
				4.2	1.0093	0.4161				4.4	1.017	0.4326			
				4.7	1.0064	0.4670				4.1	1.009	0.4063			
				4.4	1.0225	0.4303				3.9	1.064	0.3665			
				3.8	1.0194	0.3728				4.6	1.093	0.4209			
				4.0	1.0079	0.3969				3.6	1.014	0.3550			
				4.3	1.0124	0.4247				3.4	1.027	0.3311			
5100C	5.0	0.05	0.0196	5.3	1.0128	0.5233	0.0215	0.068	0.1192	5.6	1.165	0.4807	0.053	0.17	
				5.0	1.0093	0.4954				5.0	1.017	0.4916			
				5.5	1.0064	0.5465				5.4	1.009	0.5352			
				5.5	1.0225	0.5379				4.1	1.064	0.3853			
				5.1	1.0194	0.5003				4.5	1.093	0.4117			
				5.0	1.0079	0.4961				4.6	1.014	0.4536			
				5.4	1.0124	0.5334				5.2	1.027	0.5063			
4100	5.0	0.05	0.0000	4.2	1.0128	0.4147	0.0335	0.105	0.0550	4.6	1.165	0.3948	0.040	0.13	
				4.8	1.0093	0.4756				4.2	1.017	0.4130			
				4.9	1.0064	0.4869				5.0	1.009	0.4955			
				4.9	1.0225	0.4792				4.2	1.064	0.3947			
				4.9	1.0194	0.4807				4.1	1.093	0.3751			
				4.1	1.0079	0.4068				4.5	1.014	0.4438			
				4.5	1.0124	0.4445				4.2	1.027	0.4090			

Reference: 40 CFR 136, Appendix B (ERA Inorganic Blank Sand & AEC Standard Soil)/SW846

GMDLSOIL

LEAD BY GFAA
(USAEC METHOD GPB1)

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **ANALYSIS OF AQUEOUS SAMPLES FOR LEAD BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7421) USAEC METHOD - GPB1 - WATER**

TABLE OF CONTENTS

TITLE: **ANALYSIS OF AQUEOUS SAMPLES FOR LEAD BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7421) USAEC METHOD - GPB1 - WATER**

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental aqueous samples and wastes with suspended solids for lead (Pb) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Aqueous samples for GFAAS determination of lead are digested by EPA SW-846 Method 3020 and analyzed by EPA SW-846 Method 7421.

1.2.2 There are two deviations from the SW-846 method: a) the initial and final volume of sample digested is 50 mL instead of 100 mL and b) the use of palladium nitrate as a matrix modifier instead of phosphoric acid based on the instrument manufacturer's recommendations.

1.2.3 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at approximately twice the reporting limit and two spikes at approximately twenty times the reporting limit will be digested and analyzed with each lot of samples.

1.2.4 A representative 50 mL aliquot of sample is prepared for analysis by refluxing on a hot plate with nitric acid in a covered beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. The digestate is then cooled, filtered and diluted to 50 mL.

1.2.5 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of light at a specific wavelength during atomization is measured and the concentration of lead in the sample is calculated based on the instrument's calibration curve. Element specific instrument conditions are listed in section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annual and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for lead in aqueous samples are reported below:

Element	MDL (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)
Lead	2.0	2.0	100

1.4. INTERFERENCES

1.4.1 Laboratory control samples are used to verify that the digestion procedure was appropriate. A matrix modifier is added to the sample to minimize volatilization losses during the drying and ashing steps of the graphite furnace temperature program and to minimize matrix interferences (the Perkin-Elmer Model 4100ZL does not routinely require the use of a matrix modifier).

1.4.2 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of aqueous samples with nitric acid which is corrosive. Adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain nitric acid, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;

2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;

2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;

2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);

2.1.5 Disposable beakers, 10-mL capacity;

2.1.6 Class A volumetric flasks (1000 mL, 200 mL, 100 mL);

2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);

2.1.8 Graduated cylinders (50 mL);

2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;

2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer instrument equipped with a Model HGA-600 graphite furnace, Zeeman background correction, an electrodeless discharge lamp (EDL) or hollow cathode lamp (HCL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube with L'vov platform;

2.2.2 Purge gas - Argon, 99.9% pure;

2.2.3 Matrix modifier (5100Z) - 500 ppm palladium nitrate;

2.2.4 Matrix modifier (4100ZL) - none;

2.2.5 Sample injection volume - 20 uL;

2.2.6 Matrix modifier injection volume (5100Z) - 5 uL;

2.2.7 Duplicate burns for all standards and samples with the average reported as the final result;

2.2.8 Wavelength - 283.3 nanometers (nm);

2.2.9 Slitwidth - 0.7 nm.

2.2.10 Lead furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	2-10	20-60
	2	300-500	2-20	10-40
	3	1800-2100	0-5	3-10
	4	2300-2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	600-900	3-20	20-60
	3	1800-2100	0-5	3-10
	4	2500-2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).

Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.

Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.

Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.

Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.

2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.

2.3.3 Nitric acid (1+1) - using a 100 mL graduated cylinder, 100 mL of conc. HNO_3 is added to 100 mL deionized water and placed in a nalgene dispenser bottle.

2.3.4 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.5 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 Pb standard solution: Use a commercially purchased 1,000 milligram-per-liter (mg/L) stock solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Lead Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L lead stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 100 $\mu g/L$ Lead Standard (C2): Using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L lead intermediate (C1) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 $\mu g/L$ Lead Standard (C3): Using a volumetric pipet, 10 mL of the 100 $\mu g/L$ lead standard (C2) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 100 $\mu g/L$ and 10 $\mu g/L$ lead standards with a 5% HNO_3 solution (see Sec. 3.1).

2.4.6 5 mg/L Lead Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L lead stock is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NIST reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 50 ug/L Pb continuing calibration verification solution (CCV): using a volumetric pipet transfer 1.0 mL of the 10 mg/L lead intermediate (C1) is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 5-percent HNO_3 solution: using a Nalgene dispenser bottle, 5 mL conc. HNO_3 is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for Pb is 7739-92-1, its atomic weight is 207.19 and density 11.34 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

100 ug/L and 10 ug/L lead standards are prepared as outlined in Sec. 2.4. Additional calibration standards for Pb are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Lead

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	100	20	0	100
C2	100	10	10	50
C2	100	5	15	25
C3	10	20	0	10
C3	10	4	16	2.0
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for Pb by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 100 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (50 ug/L Pb) is reanalyzed. If the measured concentration for this standard is not $\pm$ 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Aqueous samples for metals analysis must be preserved with nitric acid to a pH of less than 2. The pH of the sample should be checked after addition to the container to insure that the pH is less than or equal to 2, and more acid added if necessary.

4.2 SAMPLING CONTAINERS

Aqueous samples are taken in one liter polypropylene bottles with screw caps.

4.3 STORAGE CONDITIONS

Samples are shipped to and stored in the laboratory at room temperature.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 PROCEDURE

5.1. SAMPLE DIGESTION

5.1.1 Using a graduated cylinder, transfer a 50 mL aliquot of well-mixed sample to a 150 mL beaker or erlenmeyer flask. Add 1.5 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 1.5 mL portion of concentrated HNO_3. Cover the beaker with a non-ribbed watch glass, return to the hot plate and gently reflux.

5.1.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL) using a ribbed watch glass and not allowing any portion of the bottom of the beaker to do dry. Remove the beaker and add approximately 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

5.1.3 Remove the beaker and allow to cool. Wash down the beaker walls with Type I water and filter, if necessary. Filtration should be done only if there is concern that insoluble material may clog the autosampler. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute HNO_3 prior to use.

5.1.4 Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 5% (v/v) HNO_3.

5.1.5 Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.6 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.7 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.8 Enter the digestion date in the computer.

5.1.9 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7421 (1986).

5.2.5 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported lead concentration for that sample should be qualified as having a possible interference.

5.2.6 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.7 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.8 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.9 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.10 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.11 When MSA is required, four 5.0 mL aliquots of sample are spiked with 0, 20, 40, and 60 uL respectively of a 5.0 mg/L Pb solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (cc) for each set. If the cc is less than 0.995, repeat the analysis once. If the cc is still less than 0.995, the original sample response will be reported and qualified as having a possible interference.

5.2.12 Attachment 3 shows a typical GFAA run sequence.

6.0 CALCULATIONS

6.1 The Perkin-Elmer 5100Z and 4100ZL instruments determine the absorbance-seconds of Pb in the sample digestate and calculate the sample concentration in ug/L directly from the standard curve. If the sample concentration of Pb is within the calibration range, the sample concentration will be reported as as calculated by the instrument. If the concentration of Pb is either not detected or below the method detection limit, the sample concentration will be reported as less than the method detection limit. If the concentration of Pb is greater than the highest calibration standard, the sample digestate should be diluted within range and reanalyzed. The concentration in the diluted sample and the dilution factor are reported. The highest calibration range for Pb is 100 ug/L as given in Sec. 1.3. When MSA is performed, the result from this analysis will be used unless the cc <0.995.

6.2 Post digestion spikes (SPX) are prepared by adding one part high standard (100 ug/L) to one part sample. A dilution factor of two is entered in the data batch and the target concentration will equal the concentration of the high standard (100 ug/L).

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, 0.5 mL of 1000 ppm stock standard that is commercially purchased is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 500 ug-Pb/L. This solution is prepared fresh monthly (see Section 2.4.10 for policy on stock standard source).

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 50 mL of deionized water:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)
Blank	--	0
Low	0.5	5.0
High	5.0	50.0
High	5.0	50.0

7.1.3 When required, sample matrix spikes are prepared by adding 5.0 mL of the spike solution to 2-50 mL aliquots of the sample. The target concentration will be 50 ug/L.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.
2. Difference between the two high concentration spiked QC samples in each lot.
3. Three-point moving average percent recovery for the low level spike in each lot.
4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.5 EPA Method 7421 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.6 EPA Method 3020 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

October 27, 1993

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (Pb, Tl, & V)	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of Pb & Tl 1000 ppm stock standards and 1.0 mL of V 1000 ppm stock standard are transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for Pb & Tl and 1000 ug/L for V. This solution is prepared fresh monthly.

2. Prepare quality control samples:
   a. Method blank (MB) - reagents only.
   b. Low spike (SP1) - add 0.5 mL of spike solution to 50 mL DI.
   c. High spike (SP2, SP3)- add 5.0 mL of spike solution to 2-50 mL aliquots of DI.
   d. Sample matrix spikes (SPM1, SPM2)- add 5.0 mL of spike solution to 2-50 mL aliquots of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
Pb, Tl	5 ug/L	50 ug/L	50 ug/L
V	10 ug/L	100 ug/L	100 ug/L

DIGESTION PROCEDURE:

1. Using a graduated cylinder, transfer a 50 mL aliquot of sample to a 150 mL beaker or erlenmeyer flask. Add 1.5 mL of conc HNO_3. Cover with a ribbed watch glass. Place on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool and add another 1.5 mL portion of conc. HNO_3. Cover with a non-ribbed watch glass, return to the hot plate and gently reflux.

2. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL) using a ribbed watch glass and not allowing any portion of the bottom of the beaker to do dry. Remove the beaker and add approx. 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

3. Remove and cool. Wash down the beaker walls with Type I water and filter, if necessary.

4. Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 5% (v/v) HNO_3.

5. Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

6. Enter the digestion date in the computer.

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (Pb, Tl & V)	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.

2. Prepare the following standards for instrument dilution (Note: standards should be 5% HNO_3):

Element	Conc.(ug/L)	Calibration Curves (ug/L)
Pb	100 & 10	100, 50, 25, 10, 2.0, 0.0
Tl	100 & 10	100, 50, 25, 10, 2.5, 0.0
V	200 & 10	200, 100, 50, 10, 5.0, 0.0

3. Method detection limits (MDL):
   Pb = 2.0 ug/L   Tl = 2.5 ug/L   V = 5.0 ug/L
4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.

5. Analyze the standard curve. The cc must be > 0.995.

6. Analyze the ICV. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

7. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.

8. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD is greater than 20% for a sample whose concentration exceeds twice the MDL, reanalyze the sample. If RPD is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.

9. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

10. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

11. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not ± 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L MSA solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (Pb, Tl & V)	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS (Chemical Laboratory Analysis and Scheduling System) data batch. CLASS is ESE's computerized data management system.

2. If the method blank has a response greater than the instrument detection limit the data must be reviewed by the department manager to determine is the data is acceptable.

3. If the method blank (or any sample with a SPM or SPX) has a response less than the instrument detection limit, enter the response as 0 Final so that CLASS will not use the response in the recovery calculations.

4. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.

5. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 - TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank	
Standard 1 (2.5 ug/L)	
Standard 2 (10.0 ug/L)	
Standard 3 (25.0 ug/L)	
Standard 4 (50.0 ug/L)	
Standard 5 (100 ug/L)	
Initial calibration verification - ICV (reference)	± 10%
Method blank (MB)	
Low spike (SP1)	see control charts
High spike (SP2)	see control charts
High spike (SP3)	see control charts
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike dup	
Sample #2	
CCV (50 ug/L)	± 10%
Continuing calibration blank - CCB	
Sample #3 through #12	
CCV (50 ug/L)	± 10%
CCB	
Sample #13 through #20	
Serial Dilution (1+4)	± 10%
or Post-Digestion Spike (SPX)	± 15%
CCV (50 ug/L)	± 10%
CCB	
MSA - 0	
MSA - 1	
MSA - 2	
MSA - 3	
CCV (50 ug/L)	± 10%
CCB	

ATTACHMENT 3.0 - MDL STUDY

October 27, 1993

GFAA Instrument & Method Detection Limits
JANUARY 1993

Element	Spike Conc. (ug/L)	Day 1 Response (ug/L)	Day 1 SD (ug/L)	Day 2 Response (ug/L)	Day 2 SD (ug/L)	Day 3 Response (ug/L)	Day 3 SD (ug/L)	IDL (ug/L)	Combined Reported IDL (ug/L)	Unspiked Response (ug/L)	Spiked Response (ug/L)	MDL (ug/L)	Combined Reported MDL (ug/L)
Lead	5.0	6.4	0.20	3.7	0.20	6.3	0.30	0.7	1.5	0.0	7.1	1.4	2.0
5100A		6.3		4.0		5.9					5.2		
		6.6		3.6		6.5					4.1		
		6.1		4.0		6.0					4.9		
		6.6		3.9		5.9					8.2		
		6.3		3.8		5.8					5.7		
		6.6		3.5		6.5					5.6		
5100B	5.0	6.4	0.28	6.5	0.20	6.0	0.13	0.6		0.1	7.1	1.2	
		6.5		6.2		6.0					5.4		
		5.9		6.0		6.2					4.3		
		6.2		6.1		6.1					5.1		
		6.7		6.2		6.2					7.6		
		6.2		5.9		5.9					5.1		
		6.0		6.0		5.9					5.1		
5100C	5.0	5.9	0.17	7.9	0.26	5.3	0.20	0.6		0.3	7.2	1.3	
		5.8		7.7		4.9					5.7		
		5.8		7.9		5.4					4.6		
		5.9		7.2		5.3					5.4		
		5.7		7.5		5.0					8.4		
		5.4		7.5		5.4					5.9		
		5.8		7.8		5.1					5.4		
4100	5.0	5.7	0.14	4.9	0.17	4.4	0.19	0.5		0.3	7.3	1.2	
		5.9		5.2		4.0					5.8		
		5.6		5.3		4.4					4.8		
		5.8		5.4		4.2					5.4		
		5.5		5.0		4.5					8.3		
		5.8		5.2		4.1					6.2		
		5.6		5.2		4.1					5.4		

Reference: CLP390 (ILM01.0) & 40 CFR 136, App. B/SW846

GFAADL

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: ANALYSIS OF SOIL AND SEDIMENT SAMPLES FOR LEAD BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3050/7421) USAEC METHOD - GPB1 - SOIL

TABLE OF CONTENTS

TITLE: **ANALYSIS OF SOIL AND SEDIMENT SAMPLES FOR LEAD BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3050/7421) USAEC METHOD - GPB1 - SOIL**

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental soil and sediment samples for lead (Pb) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Soil and sediment samples for GFAAS determination are digested by EPA SW-846 Method 3050 and analyzed following EPA SW-846 Method 7421. The only deviation from these methods is the use of palladium nitrate as a matrix modifier instead of phosphoric acid based on the instrument manufacturer's recommendations.

1.2.2 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at the reporting limit and two spikes at ten times the reporting limit will be digested and analyzed with each lot of samples. These concentrations deviate from the requirements of twice and twenty times the MDL due to the high background of the standard soil.

1.2.3 A representative 1-2 g (wet weight) sample is prepared for analysis by refluxing on a hot plate at approximately 95°C with a mixture of nitric acid and hydrogen peroxide in a covered beaker. The digestate is then cooled, filtered and diluted to 100 mL.

1.2.4 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of light at a specific wavelength during atomization is measured and the concentration of lead in the sample is calculated based on the instrument's calibration curve. Element specific instrument conditions are listed in section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annual and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for lead in soil and sediment samples are reported below:

Element	MDL (ug/g)	Lower Standard Range (ug/g)⁺	Upper Standard Range (ug/g)⁺
Lead	0.50	0.25	10.0

⁺ Based on 1 g of soil and 100 mL final volume

1.4. INTERFERENCES

1.4.1 Laboratory control samples are used to verify that the digestion procedure was appropriate. A matrix modifier is added to the sample to minimize matrix interferences (the Perkin-Elmer Model 4100 ZL does not routinely require the use of a matrix modifier).

1.4.2 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of soil and sediment samples with a mixture of nitric acid and 30 percent hydrogen peroxide. Both of these reagents are corrosive, and adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain nitric acid, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;
2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;
2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;
2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);
2.1.5 Disposable beakers, 10-mL capacity;
2.1.6 Class A volumetric flasks (1000 mL, 200 mL, 100 mL);
2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);
2.1.8 Graduated cylinders (100 mL);
2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;
2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer instrument equipped with a Model HGA-600 graphite furnace, Zeeman background correction, an electrodeless discharge lamp (EDL) or hollow cathode lamp (HCL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube with L'vov platform;
2.2.2 Purge gas - Argon, 99.9% pure;
2.2.3 Matrix modifier (5100Z) - 500 ppm palladium nitrate;
2.2.4 Matrix modifier (4100ZL) - none;
2.2.5 Sample injection volume - 20 uL;
2.2.6 Matrix modifier injection volume - 5 uL;
2.2.7 Duplicate burns for all standards and samples with the average reported as the final result;
2.2.8 Wavelength - 283.3 nanometers (nm);
2.2.9 Slitwidth - 0.7 nm.

2.2.10 Lead furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	2-10	20-60
	2	300-500	2-20	10-40
	3	1800-2100	0-5	3-10
	4	2300-2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	600-900	3-20	20-60
	3	1800-2100	0-5	3-10
	4	2500-2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is

complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).
Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.
Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.
Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.
Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.
2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.
2.3.3 Hydrogen Peroxide (H_2O_2) - 30 percent, trace metals grade.
2.3.4 Nitric acid (1+1) - using a 100 mL graduated cylinder, 100 mL of conc. HNO_3 is added to 100 mL deionized water and placed in a nalgene dispenser bottle.
2.3.5 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.6 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.3.7 USAEC Standard Soil.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 Pb standard solution: Use a commercially purchased 1,000 milligram-per-liter (mg/L) stock solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Lead Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L lead stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 100 μg/L Lead Standard (C2): Using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L lead intermediate (C1) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 μg/L Lead Standard (C3): Using a volumetric pipet, 10 mL of the 100 μg/L Lead standard (C2) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 100 μg/L and 10 μg/L lead standards with a 5% HNO_3 solution (see Sec. 3.1).

2.4.6 5 mg/L Lead Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L lead stock is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NIST reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 50 ug/L Pb continuing calibration verification solution (CCV): using a volumetric pipet transfer 1.0 mL of the 10 mg/L lead intermediate (C1) is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 5-percent HNO_3 solution: using a Nalgene dispenser bottle, 5 mL conc. HNO_3 is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for Pb is 7739-92-1, its atomic weight is 207.19 and density 11.34 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

100 ug/L and 10 ug/L lead standards are prepared as outlined in Sec. 2.4. Additional calibration standards for Pb are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Lead

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	100	20	0	100
C2	100	10	10	50
C2	100	5	15	25
C3	10	20	0	10
C3	10	5	15	2.5
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for Pb by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 100 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (50 ug/L Pb) is reanalyzed. If the measured concentration for this standard is not $\pm$ 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Soil and sediment samples for metals analysis must be maintained in a temperature-controlled room at 4 degrees Celsius (°C).

4.2 SAMPLING CONTAINERS

Environmental soil and sediment samples are collected in wide-mouth, amber-glass jars with teflon-lined lids.

4.3 STORAGE CONDITIONS

Samples are shipped and stored in the laboratory at 4° C.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 PROCEDURE

5.1. SAMPLE DIGESTION

5.1.1 Mix the sample thoroughly to achieve homogeneity. Weigh directly into a beaker or erlenmeyer flask, a 1 to 2 g aliquot of sample to the nearest 0.0001 g. For samples with low percent solids a larger sample size may be necessary.

5.1.2 Add 10 mL of 1+1 HNO_3 and mix the slurry. The sample is covered with a non-ribbed watch glass and refluxed on a hot plate at 95°C for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.

5.1.3 Allow the sample to cool and add 2 mL Type I water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool.

5.1.4 Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than a total 10 mL of 30% H_2O_2.

5.1.5 Cover the beaker with a ribbed watch glass and continue heating until the volume has been reduced to approximately 5 mL. Remove the beaker and allow the sample to cool. Wash down the beaker walls with Type I water and filter or centrifuge the sample to remove particulates that could clog the GFAA autosampler during analyses. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute nitric acid prior to use.

5.1.6 Adjust the final volume to 100 mL with Type I water. The digested sample will have an approximate acid concentration of 5% (v/v) HNO_3.

5.1.7 A reagent blank should also be carried through the entire digestion procedure.

5.1.8 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.9 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.10 Enter the digestion date and sample weights in the computer.

5.1.11 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the reagent blank. If the reagent blank is greater than twice the method detection limit, the samples must be redigested and the newly prepared samples analyzed or an adequate explanation provided as to why the original samples should be acceptable.

5.2.5 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7421 (1986).

5.2.6 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported lead concentration for that sample should be qualified as having a possible interference.

5.2.7 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.8 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.9 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within $\pm$ 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.10 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.11 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.12 When MSA is required, four 5.0 mL aliquots of sample are spiked with 0, 20, 40, and 60 uL respectively of a 5.0 mg/L Pb solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (cc) for each set. If the cc is less than 0.995, repeat the analysis once. If the cc is still less than 0.995, the original sample response will be reported and qualified as having a possible interference.

5.2.13 Attachment 3 shows a typical GFAA run sequence.

6.0 CALCULATIONS

6.1 The Perkin-Elmer 5100Z and 4100ZL instruments determine the absorbance-seconds of Pb in the sample digestate and calculate the sample concentration in ug/L directly from the standard curve. If the sample concentration of Pb is within the calibration range, the sample concentration will be reported as calculated from Sec.6.2. If the concentration of Pb is either not detected or below the method detection limit, the sample concentration will be reported as less than the method detection limit. If the concentration of Pb is greater than the highest calibration standard, the sample digestate should be diluted within range and reanalyzed. The concentration in the diluted sample and the dilution factor are reported. The highest calibration range for Pb is 10.0 ug/g (100 ug/L) as given in Sec. 1.3. When MSA is performed, the result from this analysis will be used unless the cc <0.995.

6.2 For soils and sediments, the measured ug/L concentration or MSA value, digested sample weight and percent solids are entered in the data batch. If a dilution was required, the concentration in the diluted sample and the dilution factor are entered in the data batch. Dry weight results are based on the following calculation:

$$\text{Conc, dry (ug/g)} = \frac{\text{Conc. in digestate (ug/L) x Digestate vol. (L)}}{\text{Wet weight of sample (g) x \% solids}}$$

6.3 Post digestion spikes (SPX) are prepared by adding one part high standard (100 ug/L) to one part sample. A dilution factor of two is entered in the data batch and the target concentration will equal the concentration of the high standard (100 ug/L).

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, .8 mL of 1000 ppm stock standard solution that is commercially purchased is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 800 ug-Pb/L. This solution is prepared fresh monthly (see Section 2.4.10 for policy on stock standard source).

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 0.1 g of standard soil:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)	Conc. of Control Spike (ug/g)+
Blank	--	0	0
Low	1.0	8.0	0.8
High	10.0	80	8.0
High	10.0	80	8.0

+ Note: ug/g target concentrations for control spikes are based on 1.0 g. The actual weight of standard soil used is multiplied by 10 per USAEC instructions.

7.1.3 When required, sample matrix spikes are prepared by adding 10.0 mL of the spike solution to 2-1.0 g portions of the sample. The target concentration will be 5.0 ug/g.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.
2. Difference between the two high concentration spiked QC samples in each lot.
3. Three-point moving average percent recovery for the low level spike in each lot.

4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 3050 - Test Methods for Evaluating Solid Wastes, EPA SW 846, 3rd Edition, September 1986.

8.5 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.6 EPA Method 7421 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of As, Se, & Tl 1000 ppm stock standards 0.8 mL of Pb 1000 ppm stock standard, and 1.0 mL of V 1000 ppm stock standard are transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for As, Se, & Tl, 800 ug/L for Pb and 1000 ug/L for V. This solution is prepared fresh monthly.
2. Prepare quality control samples:
   a. Reagent blank - reagents only.
   b. Method blank (MB) - 0.1 g portion of standard soil plus reagents.
   c. Low spike (SP1) - add 1.0 mL of spike solution to 0.1 g portion of standard soil.
   d. High spike (SP2,SP3)- add 10.0 mL of spike solution to 2-0.1 g portions of standard soil.
   e. Sample matrix spikes (SPM1, SPM2)- add 10.0 mL of spike solution to 2-1.0 g portions of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
As, Se, Tl	0.5 ug/g (5 ug/L)	5.0 ug/g (50 ug/L)	5.0 ug/g (50 ug/L)
Pb	0.8 ug/g (8 ug/L)	8.0 ug/g (80 ug/L)	8.0 ug/g (80 ug/L)
V	1.0 ug/g (10 ug/L)	10.0 ug/g (100 ug/L)	10.0 ug/g (100 ug/L)

Note: ug/g target concentrations for low and high spike are based on 1.0 g.

DIGESTION PROCEDURE:

1. Mix the sample thoroughly. Weigh into a beaker or erlenmeyer flask, a 1-2 g aliquot of sample to the nearest 0.0001 g. For samples with low % solids a larger sample size may be necessary.
2. Add 10 mL of 1+1 HNO_3 and mix. Cover with a non-ribbed watch glass and reflux on a hot plate at 95°C for 10-15 minutes without boiling. Cool the sample, and add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.
3. Allow the sample to cool. Add 2 mL Type I water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool. Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or the general appearance is unchanged. Do not add more than a total 10 mL of H_2O_2.
4. Cover with a ribbed watch glass and continue heating until the volume has been reduced to approx. 5 mL. Remove the beaker and allow to cool. Wash down the beaker walls with deionized water and filter if necessary. Adjust the final volume to 100 mL with Type II water. The digested sample will have an approximate acid concentration of 5% (v/v) HNO_3.
5. Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.
6. Enter the digestion date and sample weights in the computer.

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.
2. Prepare the following standards for instrument dilution (Note: standards should be 5% HNO_3):

Element	Conc.(ug/L)	Calibration Curves (ug/L)
As,Pb,Se,Tl	100 & 10	100, 50, 25, 10, 2.5, 0.0
V	200 & 10	200, 100, 50, 10, 5.0, 0.0

3. Method detection limits (MDL):
   As = 0.25 ug/g (2.5 ug/L) Tl = 0.25 ug/g (2.5 ug/L)
   Pb = 0.50 ug/g (5.0 ug/L) V = 0.75 ug/g (7.5 ug/L)
   Se = 0.25 ug/g (2.5 ug/L)
4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.
5. Analyze the standard curve. The cc must be > 0.995.
6. Analyze the ICV. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.
7. Analyze the reagent blank. If the reagent blank is greater than twice the MDL, redigest the samples or provide an adequate explanation as to why the samples should be acceptable.
8. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.
9. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, reanalyze the sample. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.
10. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.
11. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.
12. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L MSA solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS (Chemical Laboratory Analysis and Scheduling System) data batch. CLASS is ESE's computerized data management system.
2. If the method blank has a response greater than the instrument detection limit, blank correction should be applied to the daily control spikes only. If the MB (or any sample with a matrix spike) has a negative response or is less than the instrument detection limit, enter the response as 0 Final.
3. Use 10X the actual standard soil weight for the method blank and control spike calculations.
4. Digestate volumes (0.1 L), weights (g) and % moisture should be supplied by CLASS. Verify the entries are correct. Responses should be uploaded in ug/L. (% Moisture for standard soil = 0.05). Include the sample %moisture summary in the data batch.
5. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.
6. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 - TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank		
Standard 1 (2.5 ug/L)		
Standard 2 (10.0 ug/L)		
Standard 3 (25.0 ug/L)		
Standard 4 (50.0 ug/L)		
Standard 5 (100 ug/L)		
Initial calibration verification - ICV (reference)		± 10%
Reagent blank		
Method blank (MB)		
Low spike (SP1)	see control charts	
High spike (SP2)	see control charts	
High spike (SP3)	see control charts	
Sample #1		
Sample #1 matrix spike		
Sample #1 matrix spike dup		
Sample #2		
CCV (50 ug/L)		± 10%
Continuing calibration blank - CCB		
Sample #3 through #12		
CCV (50 ug/L)		± 10%
CCB		
Sample #13 through #20		
Serial Dilution (1+4)		± 10%
or Post-Digestion Spike (SPX)		± 15%
CCV (50 ug/L)		± 10%
CCB		
MSA - 0		
MSA - 1		
MSA - 2		
MSA - 3		
CCV (50 ug/L)		± 10%
CCB		

ATTACHMENT 3.0 - MDL STUDY

October 27, 1993

GFAA Soil/Sediment MDL Study
January 1993

Element	Spike Conc. (ug/L)	Spike Conc. (ug/g)	ERA-Unspiked Response (ug/g)	ERA-Spike Response (ug/L)	ERA-Spike Weight (g)	ERA-Spike Response (ug/g)	Standard Deviation (ug/g)	ERA Soil MDL (ug/g)	AEC-Unspiked Response (ug/g)	AEC-Spike Response (ug/L)	AEC-Spike Weight (g)x10	AEC-Spike Response (ug/g)	Standard Deviation (ug/g)	AEC Soil MDL (ug/g)	Combined Reported MDL (ug/~~L~~g)
Lead	5.0	0.05	0.0391	5.0	1.0128	0.4937	0.0152	0.048	0.4033	12.3	1.165	1.0558	0.148	0.46	0.50
5100A				5.3	1.0093	0.5251				9.5	1.017	0.9341			
				5.3	1.0064	0.5266				9.8	1.009	0.9713			
				5.3	1.0225	0.5183				10.6	1.064	0.9962			
				5.0	1.0194	0.4905				10.9	1.093	0.9973			
				5.1	1.0079	0.5060				9.4	1.014	0.9270			
				5.3	1.0124	0.5235				13.9	1.027	1.3535			
5100B	5.0	0.05	0.0293	4.7	1.0128	0.4641	0.0159	0.050	0.3666	14.4	1.165	1.2361	0.122	0.38	
				5.1	1.0093	0.5053				11.1	1.017	1.0914			
				4.7	1.0064	0.4670				11.1	1.009	1.1001			
				4.8	1.0225	0.4694				11.0	1.064	1.0338			
				4.7	1.0194	0.4611				11.2	1.093	1.0247			
				4.9	1.0079	0.4862				10.7	1.014	1.0552			
				4.9	1.0124	0.4840				13.9	1.027	1.3535			
5100C	5.0	0.05	0.0391	5.2	1.0128	0.5134	0.0218	0.068	0.3483	15.8	1.165	1.3562	0.106	0.33	
				5.5	1.0093	0.5449				12.0	1.017	1.1799			
				5.3	1.0064	0.5266				11.9	1.009	1.1794			
				5.2	1.0225	0.5086				11.9	1.064	1.1184			
				5.0	1.0194	0.4905				11.9	1.093	1.0887			
				4.9	1.0079	0.4862				12.0	1.014	1.1834			
				5.4	1.0124	0.5334				13.9	1.027	1.3535			
4100	5.0	0.05	0.0782	5.6	1.0128	0.5529	0.0412	0.129	0.4216	16.4	1.165	1.4077	0.110	0.34	
				5.7	1.0093	0.5647				12.2	1.017	1.1996			
				5.7	1.0064	0.5664				12.3	1.009	1.2190			
				5.5	1.0225	0.5379				11.9	1.064	1.1184			
				5.4	1.0194	0.5297				12.3	1.093	1.1253			
				6.6	1.0079	0.6548				12.2	1.014	1.2032			
				5.8	1.0124	0.5729				13.9	1.027	1.3535			

Reference: 40 CFR 136, Appendix B (ERA Inorganic Blank Sand & AEC Standard Soil)/SW846

GMDLSOIL

ANTIMONY BY GFAA
(USAEC METHOD GSB1)

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **ANALYSIS OF AQUEOUS SAMPLES FOR ANTIMONY BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7041)
USAEC METHOD - GSB1 - WATER**

TABLE OF CONTENTS

TITLE: ANALYSIS OF AQUEOUS SAMPLES FOR ANTIMONY BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7041) USAEC METHOD - GSB1 - WATER

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental aqueous samples and wastes with suspended solids for antimony (Sb) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Aqueous samples for GFAAS determination are digested by EPA SW-846 Method 3005 and analyzed following EPA SW-846 Method 7041.

1.2.2 The only deviation from these methods is the initial and final volume of sample digested is 50 mL instead of 100 mL.

1.2.3 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at twice the reporting limit and two spikes at twenty times the reporting limit will be digested and analyzed with each lot of samples.

1.2.4 A representative 50 mL aliquot of sample is prepared for analysis by refluxing on a hot plate at approximately 95°C with a mixture of nitric acid and hydrochloric acid in a covered beaker. The digestate is then cooled, filtered and diluted to 50 mL.

1.2.5 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of light at a specific wavelength during atomization is measured and the

concentration of antimony in the sample is calculated based on the instrument's calibration curve. Element specific instrument conditions are listed in section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annual and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for antimony in aqueous samples are reported below:

Element	MDL (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)
Antimony	3.0	2.5	100

1.4. INTERFERENCES

1.4.1 Elemental antimony and many of its compounds are volatile; therefore, samples may be subject to losses of antimony during sample digestion. Laboratory control samples are used to verify that the digestion procedure was appropriate. A matrix modifier is added to the sample to minimize volatilization losses during the drying and ashing steps of the graphite furnace temperature program and to minimize matrix interferences.

1.4.2 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. Zeeman background correction may also help to reduce certain chemical interferences such as the positive interference attributed to high concentrations of lead. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.4.3 The addition of hydrochloric acid during the digestion prevents the furnace analysis of the digestate for many other metals.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of aqueous samples with a mixture of nitric acid and hydrochloric acid. Both of these reagents are corrosive, and adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain acids, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;

2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;

2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;

2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);

2.1.5 Disposable beakers, 10-mL capacity;

2.1.6 Class A volumetric flasks (1000, 200 mL, 100 mL);

2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);

2.1.8 Graduated cylinders (50 mL);

2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;

2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer, or equivalent instrument equipped with a Model HGA-600 or equivalent graphite furnace, Zeeman background correction, an electrodeless discharge lamp (EDL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube with L'vov platform;

2.2.2 Purge gas - Argon, 99.9% pure;

2.2.3 Matrix modifier - 500 ppm palladium nitrate;

2.2.4 Sample injection volume - 20 uL;

2.2.5 Matrix modifier injection volume - 5 uL;

2.2.6 Duplicate burns for all standards and samples with the average reported as the final result;

2.2.7 Wavelength - 217.6 nanometers (nm);

2.2.8 Slitwidth - 0.7 nm.

2.2.9 Antimony furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	2-20	20-60
	2	500-800	5-20	10-40
	3	2000-2400	0-5	3-10
	4	2500-2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	800-1200	5-20	20-60
	3	2000-2400	0-5	3-10
	4	2500-2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).

Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.

Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.

Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.

Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.

2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.

2.3.3 Concentrated hydrochloric acid (HCl), trace metals grade.

2.3.4 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.5 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 Sb standard solution: Standard Analytical Reference Material (SARM) supplied by USAEC, if available, or equivalent 1,000 milligram-per-liter (mg/L) solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Antimony Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L antimony stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 100 $\mu g/L$ Antimony Standard (C2): Using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L antimony intermediate (C1) is transferred to a 100 mL volumetric flask, 2 mL conc. HNO_3 and 5 mL conc. HCl added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 $\mu g/L$ Antimony Standard (C3): Using a volumetric pipet, 10 mL of the 100 $\mu g/L$ antimony standard (C2) is transferred to a 100 mL volumetric flask, 2 mL conc. HNO_3 and 5 mL conc. HCl added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 100 $\mu g/L$ and 10 $\mu g/L$ antimony standards with a 2% HNO_3/5% HCl solution (see Sec. 3.1).

2.4.6 5 mg/L Antimony Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L antimony stock is transferred to a 200 mL volumetric flask, 4 mL conc. HNO_3 and 10 mL conc. HCl added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NBS reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 50 ug/L Sb continuing calibration verification solution (CCV): using a calibrated eppendorf pipet 1.0 mL of the 10 mg/L antimony intermediate (C1) is transferred to a 200 mL volumetric flask, 4 mL conc. HNO_3 and 10 mL conc. HCl added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 2-percent HNO_3/5-percent HCl solution: using a Nalgene dispenser bottle, 2 mL conc. HNO_3 and 5 mL conc. HCl is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 2% (v/v) HNO_3 and 5% HCl. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for Sb is 7740-36-0, its atomic weight is 121.75 and density 6.68 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

100 ug/L and 10 ug/L antimony standards are prepared as outlined in Sec. 2.4. Additional calibration standards for Sb are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Antimony

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	100	20	0	100
C2	100	10	10	50
C2	100	5	15	25
C3	10	20	0	10
C3	10	5	15	2.5
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for Sb by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 100 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (50 ug/L Sb) is reanalyzed. If the measured concentration for this standard is not ± 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Aqueous samples for metals analysis must be preserved with nitric acid to a pH of less than 2. The pH of the sample should be checked after addition to the container to insure that the pH is less than or equal to 2, and more acid added if necessary.

4.2 SAMPLING CONTAINERS

Aqueous samples are taken in one liter polypropylene bottles with screw caps.

4.3 STORAGE CONDITIONS

Samples are shipped to and stored in the laboratory at room temperature.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 PROCEDURE

5.1. SAMPLE DIGESTION

5.1.1 Using a graduated cylinder, transfer a 50 mL aliquot of well-mixed sample to a 150 mL beaker. Add 1.0 mL of concentrated HNO_3 and 2.5 mL concentrated HCl. Cover the beaker with a ribbed watch glass. Place on a hot plate and heat at 95°C until the volume is reduced to 10-15 mL. Do not allow the sample to boil. Antimony is easily lost by volitilization from hydrochloric acid media.

5.1.2 Remove the beaker and allow to cool. Wash down the beaker walls with Type I water and filter, if necessary. Filtration should be done only if there is concern that insoluble material may clog the autosampler. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute HNO_3 prior to use.

5.1.3 Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 2% (v/v) HNO_3 and 5% (v/v) HCl.

5.1.4 Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.5 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.6 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.7 Enter the digestion date in the computer.

5.1.8 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7041 (1986).

5.2.5 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported antimony concentration for that sample should be qualified as having a possible interference.

5.2.6 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.7 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.8 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.9 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.10 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.11 When MSA is required, four 5.0 mL aliquots of sample are spiked with 0, 20, 40, and 60 uL respectively of a 5.0 mg/L Sb solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (cc) for each set. If the cc is less than 0.995, repeat the analysis once. If the cc is still less than 0.995, the original sample response will be reported and qualified as having a possible interference.

5.2.12 Attachment 3 shows a typical GFAA run sequence.

6.0 CALCULATIONS

6.1 The Perkin-Elmer 5100Z and 4100ZL instruments determine the absorbance-seconds of Sb in the sample digestate and calculate the sample concentration in ug/L directly from the standard curve. If the sample concentration of Sb is within the calibration range, the sample concentration will be reported as as calculated by the instrument. If the concentration of Sb is either not detected or below the method detection limit, the sample concentration will be reported as less than the method detection limit. If the concentration of Sb is greater than the highest calibration standard, the sample digestate should be diluted within range and reanalyzed. The concentration in the diluted sample and the dilution factor are reported. The highest calibration range for Sb is 100 ug/L as given in Sec. 1.3. When MSA is performed, the result from this analysis will be used unless the cc <0.995.

6.2 Post digestion spikes (SPX) are prepared by adding one part high standard (100 ug/L) to one part sample. A dilution factor of two is entered in the data batch and the target concentration will equal the concentration of the high standard (100 ug/L).

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, 0.5 mL of 1000 ppm stock standard is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 500 ug-Sb/L. This solution is prepared fresh monthly.

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 50 mL of deionized water:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)
Blank	--	0
Low	0.5	5.0
High	5.0	50.0
High	5.0	50.0

7.1.3 When required, sample matrix spikes are prepared by adding 5.0 mL of the spike solution to 2-50 mL aliquots of the sample. The target concentration will be 50 ug/L.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.

2. Difference between the two high concentration spiked QC samples in each lot.

3. Three-point moving average percent recovery for the low level spike in each lot.

4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.5 EPA Method 7041 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.6 EPA Method 3005 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.:	Aqueous Samples for Sb by GFAA	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of Sb 1000 ppm stock standard is transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for Sb. This solution is prepared fresh monthly.

2. Prepare quality control samples:
   a. Method blank (MB) - reagents only.
   b. Low spike (SP1) - add 0.5 mL of spike solution to 50 mL DI.
   c. High spike (SP2, SP3)- add 5.0 mL of spike solution to 2-50 mL aliquots of DI.
   d. Sample matrix spikes (SPM1, SPM2)- add 5.0 mL of spike solution to 2-50 mL aliquots of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
Sb	5 ug/L	50 ug/L	50 ug/L

DIGESTION PROCEDURE:

1. Using a graduated cylinder, transfer a 50 mL aliquot of well-mixed sample to a 150 mL beaker. Add 1.0 mL of conc. HNO_3 and 2.5 mL conc. HCl. Cover the beaker with a ribbed watch glass. Place on a hot plate and heat at 95°C until the volume is reduced to 10-15 mL. Do not allow the sample to boil.

2. Remove the beaker and allow to cool. Wash down the beaker walls with Type I water and filter, if necessary. Filtration should be done only if there is concern that insoluble material may clog the autosampler. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute HNO_3 prior to use.

3. Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 2% (v/v) HNO_3 and 5% (v/v) HCl.

4. Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

5. Enter the digestion date in the computer.

Number	TITLE	QC REFERENCE
USAEC No.:	Aqueous Samples for Sb by GFAA	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.

2. Prepare the following standards for instrument dilution:
   (Note: standards should be 2% HNO_3/5% HCl)

Element	Conc.(ug/L)	Calibration Curves (ug/L)
Sb	100 & 10	100, 50, 25, 10, 2.5, 0.0

3. Method detection limits (MDL):
   Sb = 3.0 ug/L

4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.

5. Analyze the standard curve. The cc must be > 0.995.

6. Analyze the ICV. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

7. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.

8. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD is greater than 20% for a sample whose concentration exceeds twice the MDL, reanalyze the sample. If RPD is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.

9. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

10. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

11. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not ± 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L Sb solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.:	Aqueous Samples for Sb by GFAA	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS data batch.

2. If the method blank has a response greater than the instrument detection limit the data must be reviewed by the department manager to determine is the data is acceptable.

3. If the method blank (or any sample with a SPM or SPX) has a response less than the instrument detection limit, enter the response as 0 Final so that CLASS will not use the response in the recovery calculations.

4. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.

5. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 - TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank	
Standard 1 (2.5 ug/L)	
Standard 2 (10.0 ug/L)	
Standard 3 (25.0 ug/L)	
Standard 4 (50.0 ug/L)	
Standard 5 (100 ug/L)	
Initial calibration verification - ICV (reference)	± 10%
Method blank (MB)	
Low spike (SP1)	see control charts
High spike (SP2)	see control charts
High spike (SP3)	see control charts
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike dup	
Sample #2	
CCV (50 ug/L)	± 10%
Continuing calibration blank - CCB	
Sample #3 through #12	
CCV (50 ug/L)	± 10%
CCB	
Sample #13 through #20	
Serial Dilution (1+4)	± 10%
or Post-Digestion Spike (SPX)	± 15%
CCV (50 ug/L)	± 10%
CCB	
MSA - 0	
MSA - 1	
MSA - 2	
MSA - 3	
CCV (50 ug/L)	± 10%
CCB	

ATTACHMENT 3.0 - MDL STUDY

October 27, 1993

GFAA Instrument & Method Detection Limits
JANUARY 1993

Element	Spike Conc. (ug/L)	Day 1 Response (ug/L)	Day 1 SD (ug/L)	Day 2 Response (ug/L)	Day 2 SD (ug/L)	Day 3 Response (ug/L)	Day 3 SD (ug/L)	IDL (ug/L)	Combined Reported IDL (ug/L)	Unspiked Response (ug/L)	Spiked Response (ug/L)	SD	MDL (ug/L)	Combined Reported MDL (ug/L)
Antimony 5100A	10.0									0.1	9.0	0.48	1.5	3.0
											9.0			
											8.4			
											9.1			
											9.4			
											8.7			
											9.9			
5100B	10.0									0.3	10.2	0.34	1.1	
											10.6			
											10.8			
											10.8			
											11.1			
											11.1			
											10.4			
5100C	10.0									0.0	9.1	0.23	0.7	
											9.4			
											9.3			
											9.1			
											9.7			
											9.4			
											9.6			
4100	10.0									0.0	10.2	0.29	0.9	
											10.6			
											10.4			
											9.8			
											10.2			
											10.2			
											9.8			

Reference: CLP390 (ILM01.0) & 40 CFR 136, App. B/SW846

GFAADL

THALLIUM BY GFAA
(USAEC METHOD GTL1)

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: ANALYSIS OF AQUEOUS SAMPLES FOR THALLIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7841) USAEC METHOD - GTL1 - WATER

TABLE OF CONTENTS

TITLE: **ANALYSIS OF AQUEOUS SAMPLES FOR THALLIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7841) USAEC METHOD - GTL1 - WATER**

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental aqueous samples and wastes with suspended solids for thallium (Tl) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Aqueous samples for GFAAS determination of thallium are digested by EPA SW-846 Method 3020 and analyzed by EPA SW-846 Method 7841.

1.2.2 The only deviation to these methods is the initial and final volume of sample digested is 50 mL instead of 100 mL.

1.2.3 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at approximately twice the reporting limit and two spikes at approximately twenty times the reporting limit will be digested and analyzed with each lot of samples.

1.2.4 A representative 50 mL aliquot of sample is prepared for analysis by refluxing on a hot plate with nitric acid in a covered beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. The digestate is then cooled, filtered and diluted to 50 mL.

1.2.5 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of light at a specific wavelength during atomization is measured and the concentration of thallium in the sample is calculated based on the instrument's calibration curve. Element specific instrument conditions are listed in section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annual and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for thallium in aqueous samples are reported below:

Element	MDL (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)
Thallium	2.5	2.5	100

1.4. INTERFERENCES

1.4.1 Hydrochloric acid and excessive chloride will cause volatilization of thallium at low temperatures, therefore, samples may be subject to losses of thallium. Laboratory control samples are used to verify that the digestion procedure was appropriate. A matrix modifier is added to the sample to minimize volatilization losses during the drying and ashing steps of the graphite furnace temperature program and to minimize matrix interferences (the Perkin-Elmer Model 4100ZL does not routinely require the use of a matrix modifier).

1.4.2 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of aqueous samples with nitric acid which is corrosive. Adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain nitric acid, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;

2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;

2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;

2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);

2.1.5 Disposable beakers, 10-mL capacity;

2.1.6 Class A volumetric flasks (1000 mL, 200 mL, 100 mL);

2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);

2.1.8 Graduated cylinders (50 mL);

2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;

2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer instrument equipped with a Model HGA-600 graphite furnace, Zeeman background correction, an electrodeless discharge lamp (EDL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube with L'vov platform;

2.2.2 Purge gas - Argon, 99.9% pure;

2.2.3 Matrix modifier (5100Z) - 500 ppm palladium nitrate;

2.2.4 Matrix modifier (4100ZL) - none;

2.2.5 Sample injection volume - 20 uL;

2.2.6 Matrix modifier injection volume (5100Z) - 5 uL;

2.2.7 Duplicate burns for all standards and samples with the average reported as the final result;

2.2.8 Wavelength - 276.8 nanometers (nm);

2.2.9 Slitwidth - 0.7 nm.

2.2.10 Thallium furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	2-10	10-40
	2	300-500	2-20	10-40
	3	1400-1800	0-5	3-10
	4	2400-2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	300-900	3-20	20-60
	3	1400-1800	0-5	3-10
	4	2500-2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).

Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.

Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.

Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.

Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.

2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.

2.3.3 Nitric acid (1+1) - using a 100 mL graduated cylinder, 100 mL of conc. HNO_3 is added to 100 mL deionized water and placed in a nalgene dispenser bottle.

2.3.4 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.5 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 Tl standard solution: Use a commercially purchased 1,000 milligram-per-liter (mg/L) stock solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Thallium Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L thallium stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 100 μg/L Thallium Standard (C2): Using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L thallium intermediate (C1) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 μg/L Thallium Standard (C3): Using a volumetric pipet, 10 mL of the 100 μg/L thallium standard (C2) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 100 μg/L and 10 μg/L thallium standards with a 5% HNO_3 solution (see Sec. 3.1).

2.4.6 5 mg/L Thallium Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L thallium stock is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NIST reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 50 ug/L Tl continuing calibration verification solution (CCV): using a volumetric pipet transfer 1.0 mL of the 10 mg/L thallium intermediate (C1) is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 5-percent HNO_3 solution: using a Nalgene dispenser bottle, 5 mL conc. HNO_3 is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for Tl is 7740-28-0, its atomic weight is 204.37 and density 11.85 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

100 ug/L and 10 ug/L thallium standards are prepared as outlined in Sec. 2.4. Additional calibration standards for Tl are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Thallium

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	100	20	0	100
C2	100	10	10	50
C2	100	5	15	25
C3	10	20	0	10
C3	10	5	15	2.5
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for Tl by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 100 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (50 ug/L Tl) is reanalyzed. If the measured concentration for this standard is not $\pm$ 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Aqueous samples for metals analysis must be preserved with nitric acid to a pH of less than 2. The pH of the sample should be checked after addition to the container to insure that the pH is less than or equal to 2, and more acid added if necessary.

4.2 SAMPLING CONTAINERS

Aqueous samples are taken in one liter polypropylene bottles with screw caps.

4.3 STORAGE CONDITIONS

Samples are shipped to and stored in the laboratory at room temperature.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 PROCEDURE

5.1. SAMPLE DIGESTION

5.1.1 Using a graduated cylinder, transfer a 50 mL aliquot of well-mixed sample to a 150 mL beaker or erlenmeyer flask. Add 1.5 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 1.5 mL portion of concentrated HNO_3. Cover the beaker with a non-ribbed watch glass, return to the hot plate and gently reflux.

5.1.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL) using a ribbed watch glass and not allowing any portion of the bottom of the beaker to do dry. Remove the beaker and add approximately 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

5.1.3 Remove the beaker and allow to cool. Wash down the beaker walls with Type I water and filter, if necessary. Filtration should be done only if there is concern that insoluble material may clog the autosampler. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute HNO_3 prior to use.

5.1.4 Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 5% (v/v) HNO_3.

5.1.5 Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.6 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.7 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.8 Enter the digestion date in the computer.

5.1.9 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7841 (1986).

5.2.5 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported thallium concentration for that sample should be qualified as having a possible interference.

5.2.6 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.7 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.8 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within $\pm$ 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.9 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.10 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, 0.5 mL of 1000 ppm stock standard that is commercially purchased is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 500 ug-Tl/L. This solution is prepared fresh monthly (see Section 2.4.10 for policy on stock standard source).

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 50 mL of deionized water:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)
Blank	--	0
Low	0.5	5.0
High	5.0	50.0
High	5.0	50.0

7.1.3 When required, sample matrix spikes are prepared by adding 5.0 mL of the spike solution to 2-50 mL aliquots of the sample. The target concentration will be 50 ug/L.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.

2. Difference between the two high concentration spiked QC samples in each lot.

3. Three-point moving average percent recovery for the low level spike in each lot.

4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.5 EPA Method 7841 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.6 EPA Method 3020 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (Pb, Tl, & V)	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of Pb & Tl 1000 ppm stock standards and 1.0 mL of V 1000 ppm stock standard are transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for Pb & Tl and 1000 ug/L for V. This solution is prepared fresh monthly.

2. Prepare quality control samples:
   a. Method blank (MB) - reagents only.
   b. Low spike (SP1) - add 0.5 mL of spike solution to 50 mL DI.
   c. High spike (SP2, SP3)- add 5.0 mL of spike solution to 2-50 mL aliquots of DI.
   d. Sample matrix spikes (SPM1, SPM2)- add 5.0 mL of spike solution to 2-50 mL aliquots of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
Pb, Tl	5 ug/L	50 ug/L	50 ug/L
V	10 ug/L	100 ug/L	100 ug/L

DIGESTION PROCEDURE:

1. Using a graduated cylinder, transfer a 50 mL aliquot of sample to a 150 mL beaker or erlenmeyer flask. Add 1.5 mL of conc HNO_3. Cover with a ribbed watch glass. Place on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool and add another 1.5 mL portion of conc. HNO_3. Cover with a non-ribbed watch glass, return to the hot plate and gently reflux.

2. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL) using a ribbed watch glass and not allowing any portion of the bottom of the beaker to do dry. Remove the beaker and add approx. 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

3. Remove and cool. Wash down the beaker walls with Type I water and filter, if necessary.

4. Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 5% (v/v) HNO_3.

5. Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

6. Enter the digestion date in the computer.

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (Pb, Tl & V)	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.

2. Prepare the following standards for instrument dilution (Note: standards should be 5% HNO_3):

Element	Conc.(ug/L)	Calibration Curves (ug/L)
Pb	100 & 10	100, 50, 25, 10, 2.0, 0.0
Tl	100 & 10	100, 50, 25, 10, 2.5, 0.0
V	200 & 10	200, 100, 50, 10, 5.0, 0.0

3. Method detection limits (MDL):
   Pb = 2.0 ug/L Tl = 2.5 ug/L V = 5.0 ug/L
4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.

5. Analyze the standard curve. The cc must be > 0.995.

6. Analyze the ICV. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

7. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.

8. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD is greater than 20% for a sample whose concentration exceeds twice the MDL, reanalyze the sample. If RPD is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.

9. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

10. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

11. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not ± 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L MSA solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (Pb, Tl & V)	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS (Chemical Laboratory Analysis and Scheduling System) data batch. CLASS is ESE's computerized data management system.

2. If the method blank has a response greater than the instrument detection limit the data must be reviewed by the department manager to determine is the data is acceptable.

3. If the method blank (or any sample with a SPM or SPX) has a response less than the instrument detection limit, enter the response as 0 Final so that CLASS will not use the response in the recovery calculations.

4. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.

5. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 - TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank		
Standard 1 (2.5 ug/L)		
Standard 2 (10.0 ug/L)		
Standard 3 (25.0 ug/L)		
Standard 4 (50.0 ug/L)		
Standard 5 (100 ug/L)		
Initial calibration verification - ICV (reference)	± 10%	
Method blank (MB)		
Low spike (SP1)	see control charts	
High spike (SP2)	see control charts	
High spike (SP3)	see control charts	
Sample #1		
Sample #1 matrix spike		
Sample #1 matrix spike dup		
Sample #2		
CCV (50 ug/L)		± 10%
Continuing calibration blank - CCB		
Sample #3 through #12		
CCV (50 ug/L)		± 10%
CCB		
Sample #13 through #20		
Serial Dilution (1+4)	± 10%	
or Post-Digestion Spike (SPX)	± 15%	
CCV (50 ug/L)		± 10%
CCB		
MSA - 0		
MSA - 1		
MSA - 2		
MSA - 3		
CCV (50 ug/L)		± 10%
CCB		

ATTACHMENT 3.0 - MDL STUDY

October 27, 1993

GFAA Instrument & Method Detection Limits
JANUARY 1993

Element	Spike Conc. (ug/L)	Day 1 Response (ug/L)	Day 1 SD (ug/L)	Day 2 Response (ug/L)	Day 2 SD (ug/L)	Day 3 Response (ug/L)	Day 3 SD (ug/L)	IDL (ug/L)	Combined Reported IDL (ug/L)	Unspiked Response (ug/L)	Spiked Response (ug/L)	MDL (ug/L)	Combined Reported MDL (ug/L)
Thallium	10.0	8.7	0.73	10.3	0.44	10.6	0.39	1.6	2.5	0.6	8.8	0.8	2.5
5100A		8.9		9.6		11.0					9.0		
		8.5		9.1		10.0					8.9		
		8.9		9.2		10.7					9.1		
		7.2		9.6		10.3					8.7		
		8.5		9.3		10.2					8.8		
		7.3		9.0		11.0					9.5		
5100B	10.0	10.4	0.28	10.0	0.34	9.4	0.35	1.0		0.1	9.6	1.0	
		10.2		9.8		10.5					10.0		
		10.4		10.5		10.1					10.5		
		10.9		9.8		10.0					9.8		
		10.4		10.2		10.0					10.2		
		10.0		10.5		10.3					10.0		
		10.3		10.6		9.9					10.3		
5100C	10.0	9.2	0.30	10.5	0.23	9.6	0.36	0.9		0.7	10.6	1.3	
		8.7		10.6		10.3					11.3		
		9.4		10.3		9.8					11.5		
		9.7		10.7		9.7					11.5		
		9.2		10.5		9.5					10.5		
		9.4		10.0		9.2					11.2		
		9.2		10.3		9.3					11.2		
4100	10.0	8.6	0.52	10.4	0.63	11.5	1.08	2.2		0.0	10.2	2.0	
		9.3		9.6		9.9					10.5		
		9.1		10.0		10.9					9.6		
		8.0		9.9		9.8					9.7		
		7.9		9.4		8.3					9.2		
		8.7		8.9		10.6					9.4		
		8.4		10.8		11.1					8.6		

Reference: CLP390 (ILM01.0) & 40 CFR 136, App. B/SW846

GFAADL

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **ANALYSIS OF SOIL AND SEDIMENT SAMPLES FOR THALLIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3050/7841) USAEC METHOD - GTL1 - SOIL**

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TITLE: **ANALYSIS OF SOIL AND SEDIMENT SAMPLES FOR THALLIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3050/7841) USAEC METHOD - GTL1 - SOIL**

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental soil and sediment samples for thallium (Tl) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Soil and sediment samples for GFAAS determination are digested by EPA SW-846 Method 3050 and analyzed following EPA SW-846 Method 7841. The are no deviations from these methods.

1.2.2 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at twice the reporting limit and two spikes at twenty times the reporting limit will be digested and analyzed with each lot of samples.

1.2.3 A representative 1-2 g (wet weight) sample is prepared for analysis by refluxing on a hot plate at approximately 95°C with a mixture of nitric acid and hydrogen peroxide in a covered beaker. The digestate is then cooled, filtered and diluted to 100 mL.

1.2.4 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of light at a specific wavelength during atomization is measured and the concentration of thallium in the sample is calculated based on the

instrument's calibration curve. Element specific instrument conditions are listed in section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annual and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for thallium in soil and sediment samples are reported below:

Element	MDL (ug/g)	Lower Standard Range (ug/g)+	Upper Standard Range (ug/g)+
Thallium	0.25	0.25	10.0

+ Based on 1 g of soil and 100 mL final volume

1.4. INTERFERENCES

1.4.1 Hydrochloric acid and excessive chloride will cause volatilization of thallium at low temperatures, therefore, samples may be subject to losses of thallium. Laboratory control samples are used to verify that the digestion procedure was appropriate. A matrix modifier is added to the sample to minimize volatilization losses during the drying and ashing steps of the graphite furnace temperature program and to minimize matrix interferences.

1.4.2 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of soil and sediment samples with a mixture of nitric acid and 30 percent hydrogen peroxide. Both of these reagents are corrosive, and adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain nitric acid, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;

2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;

2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;

2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);

2.1.5 Disposable beakers, 10-mL capacity;

2.1.6 Class A volumetric flasks (1000 mL, 200 mL, 100 mL);

2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);

2.1.8 Graduated cylinders (100 mL);

2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;

2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer instrument equipped with a Model HGA-600 graphite furnace, Zeeman background correction, an electrodeless discharge lamp (EDL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube with L'vov platform;

2.2.2 Purge gas - Argon, 99.9% pure;

2.2.3 Matrix modifier (5100Z) - 500 ppm palladium nitrate;

2.2.4 Matrix modifier (4100ZL) - none;

2.2.5 Sample injection volume - 20 uL;

2.2.6 Matrix modifier injection volume (5100Z) - 5 uL;

2.2.7 Duplicate burns for all standards and samples with the average reported as the final result;

2.2.8 Wavelength - 276.8 nanometers (nm);

2.2.9 Slitwidth - 0.7 nm.

2.2.10 Thallium furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	2-10	10-40
	2	300-500	2-20	10-40
	3	1400-1800	0-5	3-10
	4	2400-2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	300-900	3-20	20-60
	3	1400-1800	0-5	3-10
	4	2500-2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).

Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.

Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.

Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.

Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.

2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.

2.3.3 Hydrogen Peroxide (H_2O_2) - 30 percent, trace metals grade.

2.3.4 Nitric acid (1+1) - using a 100 mL graduated cylinder, 100 mL of conc. HNO_3 is added to 100 mL deionized water and placed in a nalgene dispenser bottle.

2.3.5 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.6 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.3.7 USAEC Standard Soil.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 Tl standard solution: Use a commercially purchased 1,000 milligram-per-liter (mg/L) stock solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Thallium Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L thallium stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 100 μg/L Thallium Standard (C2): Using a calibrated Eppendorf pipet, 1.0 mL of the 10 mg/L thallium intermediate (C1) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 μg/L Thallium Standard (C3): Using a volumetric pipet, 10 mL of the 100 μg/L thallium standard (C2) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 100 μg/L and 10 μg/L thallium standards with a 5% HNO_3 solution (see Sec. 3.1).

2.4.6 5 mg/L Thallium Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L thallium stock is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NIST reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 50 ug/L Tl continuing calibration verification solution (CCV): using a volumetric pipet transfer 1.0 mL of the 10 mg/L thallium intermediate (C1) is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 5-percent HNO_3 solution: using a Nalgene dispenser bottle, 5 mL conc. HNO_3 is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for Tl is 7740-28-0, its atomic weight is 204.37 and density 11.85 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

100 ug/L and 10 ug/L thallium standards are prepared as outlined in Sec. 2.4. Additional calibration standards for Tl are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Thallium

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	100	20	0	100
C2	100	10	10	50
C2	100	5	15	25
C3	10	20	0	10
C3	10	5	15	2.5
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for Tl by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 100 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (50 ug/L Tl) is reanalyzed. If the measured concentration for this standard is not $\pm$ 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Soil and sediment samples for metals analysis must be maintained in a temperature-controlled room at 4 degrees Celsius (°C).

4.2 SAMPLING CONTAINERS

Environmental soil and sediment samples are collected in wide-mouth, amber-glass jars with teflon-lined lids.

4.3 STORAGE CONDITIONS

Samples are shipped and stored in the laboratory at 4° C.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 PROCEDURE

5.1. SAMPLE DIGESTION

5.1.1 Mix the sample thoroughly to achieve homogeneity. Weigh directly into a beaker or erlenmeyer flask, a 1 to 2 g aliquot of sample to the nearest 0.0001 g. For samples with low percent solids a larger sample size may be necessary.

5.1.2 Add 10 mL of 1+1 HNO_3 and mix the slurry. The sample is covered with a non-ribbed watch glass and refluxed on a hot plate at 95°C for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.

5.1.3 Allow the sample to cool and add 2 mL Type I water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool.

5.1.4 Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than a total 10 mL of 30% H_2O_2.

5.1.5 Cover the beaker with a ribbed watch glass and continue heating until the volume has been reduced to approximately 5 mL. Remove the beaker and allow the sample to cool. Wash down the beaker walls with Type I water and filter or centrifuge the sample to remove particulates that could clog the GFAA autosampler during analyses. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute nitric acid prior to use.

5.1.6 Adjust the final volume to 100 mL with Type I water. The digested sample will have an approximate acid concentration of 5% (v/v) HNO_3.

5.1.7 A reagent blank should also be carried through the entire digestion procedure.

5.1.8 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.9 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.10 Enter the digestion date and sample weights in the computer.

5.1.11 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the reagent blank. If the reagent blank is greater than twice the method detection limit, the samples must be redigested and the newly prepared samples analyzed or an adequate explanation provided as to why the original samples should be acceptable.

5.2.5 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7841 (1986).

5.2.6 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported thallium concentration for that sample should be qualified as having a possible interference.

5.2.7 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.8 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.9 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within $\pm$ 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.10 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.11 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.12 When MSA is required, four 5.0 mL aliquots of sample are spiked with 0, 20, 40, and 60 uL respectively of a 5.0 mg/L Tl solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (cc) for each set. If the cc is less than 0.995, repeat the analysis once. If the cc is still less than 0.995, the original sample response will be reported and qualified as having a possible interference.

5.2.13 Attachment 3 shows a typical GFAA run sequence.

6.0 CALCULATIONS

6.1 The Perkin-Elmer 5100Z and 4100ZL instruments determine the absorbance-seconds of Tl in the sample digestate and calculate the sample concentration in ug/L directly from the standard curve. If the sample concentration of Tl is within the calibration range, the sample concentration will be reported as calculated from Sec.6.2. If the concentration of Tl is either not detected or below the method detection limit, the sample concentration will be reported as less than the method detection limit. If the concentration of Tl is greater than the highest calibration standard, the sample digestate should be diluted within range and reanalyzed. The concentration in the diluted sample and the dilution factor are reported. The highest calibration range for Tl is 10.0 ug/g (100 ug/L) as given in Sec. 1.3. When MSA is performed, the result from this analysis will be used unless the cc <0.995.

6.2 For soils and sediments, the measured ug/L concentration or MSA value, digested sample weight and percent solids are entered in the data batch. If a dilution was required, the concentration in the diluted sample and the dilution factor are entered in the data batch. Dry weight results are based on the following calculation:

$$\text{Conc, dry (ug/g)} = \frac{\text{Conc. in digestate (ug/L)} \times \text{Digestate vol. (L)}}{\text{Wet weight of sample (g)} \times \text{\% solids}}$$

6.3 Post digestion spikes (SPX) are prepared by adding one part high standard (100 ug/L) to one part sample. A dilution factor of two is entered in the data batch and the target concentration will equal the concentration of the high standard (100 ug/L).

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, 0.5 mL of 1000 ppm stock standard that is commercially purchased is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 500 ug-Tl/L. This solution is prepared fresh monthly (see Section 2.4.10 for policy on stock standard source).

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 0.1 g of standard soil:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)	Conc. of Control Spike (ug/g)$^+$
Blank	--	0	0
Low	1.0	5.0	0.5
High	10.0	50.0	5.0
High	10.0	50.0	5.0

$^+$Note: ug/g target concentrations for control spikes are based on 1.0 g. The actual weight of standard soil used is multiplied by 10 per USAEC instructions.

7.1.3 When required, sample matrix spikes are prepared by adding 10.0 mL of the spike solution to 2-1.0 g portions of the sample. The target concentration will be 5.0 ug/g.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.

2. Difference between the two high concentration spiked QC samples in each lot.

3. Three-point moving average percent recovery for the low level spike in each lot.

4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 3050 - Test Methods for Evaluating Solid Wastes, EPA SW 846, 3rd Edition, September 1986.

8.5 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.6 EPA Method 7841 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

October 27, 1993

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of As, Se, & Tl 1000 ppm stock standards 0.8 mL of Pb 1000 ppm stock standard, and 1.0 mL of V 1000 ppm stock standard are transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for As, Se, & Tl, 800 ug/L for Pb and 1000 ug/L for V. This solution is prepared fresh monthly.
2. Prepare quality control samples:
   a. Reagent blank - reagents only.
   b. Method blank (MB) - 0.1 g portion of standard soil plus reagents.
   c. Low spike (SP1) - add 1.0 mL of spike solution to 0.1 g portion of standard soil.
   d. High spike (SP2,SP3)- add 10.0 mL of spike solution to 2-0.1 g portions of standard soil.
   e. Sample matrix spikes (SPM1, SPM2)- add 10.0 mL of spike solution to 2-1.0 g portions of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
As, Se, Tl	0.5 ug/g (5 ug/L)	5.0 ug/g (50 ug/L)	5.0 ug/g (50 ug/L)
Pb	0.8 ug/g (8 ug/L)	8.0 ug/g (80 ug/L)	8.0 ug/g (80 ug/L)
V	1.0 ug/g (10 ug/L)	10.0 ug/g (100 ug/L)	10.0 ug/g (100 ug/L)

Note: ug/g target concentrations for low and high spike are based on 1.0 g.

DIGESTION PROCEDURE:

1. Mix the sample thoroughly. Weigh into a beaker or erlenmeyer flask, a 1-2 g aliquot of sample to the nearest 0.0001 g. For samples with low % solids a larger sample size may be necessary.
2. Add 10 mL of 1+1 HNO_3 and mix. Cover with a non-ribbed watch glass and reflux on a hot plate at 95°C for 10-15 minutes without boiling. Cool the sample, and add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.
3. Allow the sample to cool. Add 2 mL Type I water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool. Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or the general appearance is unchanged. Do not add more than a total 10 mL of H_2O_2.
4. Cover with a ribbed watch glass and continue heating until the volume has been reduced to approx. 5 mL. Remove the beaker and allow to cool. Wash down the beaker walls with deionized water and filter if necessary. Adjust the final volume to 100 mL with Type II water. The digested sample will have an approximate acid concentration of 5% (v/v) HNO_3.
5. Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.
6. Enter the digestion date and sample weights in the computer.

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.
2. Prepare the following standards for instrument dilution (Note: standards should be 5% HNO_3):

Element	Conc.(ug/L)	Calibration Curves (ug/L)
As,Pb,Se,Tl	100 & 10	100, 50, 25, 10, 2.5, 0.0
V	200 & 10	200, 100, 50, 10, 5.0, 0.0

3. Method detection limits (MDL):
   As = 0.25 ug/g (2.5 ug/L)   Tl = 0.25 ug/g (2.5 ug/L)
   Pb = 0.50 ug/g (5.0 ug/L)   V = 0.75 ug/g (7.5 ug/L)
   Se = 0.25 ug/g (2.5 ug/L)
4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.
5. Analyze the standard curve. The cc must be > 0.995.
6. Analyze the ICV. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.
7. Analyze the reagent blank. If the reagent blank is greater than twice the MDL, redigest the samples or provide an adequate explanation as to why the samples should be acceptable.
8. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.
9. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, reanalyze the sample. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.
10. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.
11. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within ± 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.
12. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L MSA solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS (Chemical Laboratory Analysis and Scheduling System) data batch. CLASS is ESE's computerized data management system.
2. If the method blank has a response greater than the instrument detection limit, blank correction should be applied to the daily control spikes only. If the MB (or any sample with a matrix spike) has a negative response or is less than the instrument detection limit, enter the response as 0 Final.
3. Use 10X the actual standard soil weight for the method blank and control spike calculations.
4. Digestate volumes (0.1 L), weights (g) and % moisture should be supplied by CLASS. Verify the entries are correct. Responses should be uploaded in ug/L. (% Moisture for standard soil = 0.05). Include the sample %moisture summary in the data batch.
5. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.
6. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 - TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank	
Standard 1 (2.5 ug/L)	
Standard 2 (10.0 ug/L)	
Standard 3 (25.0 ug/L)	
Standard 4 (50.0 ug/L)	
Standard 5 (100 ug/L)	
Initial calibration verification - ICV (reference)	± 10%
Reagent blank	
Method blank (MB)	
Low spike (SP1)	see control charts
High spike (SP2)	see control charts
High spike (SP3)	see control charts
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike dup	
Sample #2	
CCV (50 ug/L)	± 10%
Continuing calibration blank - CCB	
Sample #3 through #12	
CCV (50 ug/L)	± 10%
CCB	
Sample #13 through #20	
Serial Dilution (1+4)	± 10%
or Post-Digestion Spike (SPX)	± 15%
CCV (50 ug/L)	± 10%
CCB	
MSA - 0	
MSA - 1	
MSA - 2	
MSA - 3	
CCV (50 ug/L)	± 10%
CCB	

ATTACHMENT 3.0 - MDL STUDY

October 27, 1993

GFAA Soil/Sediment MDL Study
January 1993

Element	Spike Conc. (ug/L)	Spike Conc. (ug/g)	ERA-Unspiked Response (ug/g)	ERA-Spike Response (ug/L)	ERA-Spike Weight (g)	ERA-Spike Response (ug/g)	Standard Deviation (ug/g)	ERA Soil MDL (ug/g)	AEC-Unspiked Response (ug/g)	AEC-Spike Response (ug/L)	AEC-Spike Weight (g)x10	AEC-Spike Response (ug/g)	Standard Deviation (ug/g)	AEC Soil MDL (ug/g)	Combined Reported MDL (ug/~~L~~g)
Thallium 5100A	10.0	0.10	0.0293	9.4	1.0128	0.9281	0.0653	0.205	0.0367	9.1	1.165	0.7811	0.056	0.18	0.25
				9.6	1.0093	0.9512				9.0	1.017	0.8850			
				10.2	1.0064	1.0135				9.0	1.009	0.8920			
				8.9	1.0225	0.8704				8.4	1.064	0.7895			
				8.4	1.0194	0.8240				8.8	1.093	0.8024			
				9.3	1.0079	0.9227				9.1	1.014	0.8974			
				10.0	1.0124	0.9878				9.3	1.027	0.9056			
5100B	10.0	0.10	0.0098	11.0	1.0128	1.0861	0.0438	0.138	0.0092	9.7	1.165	0.8326	0.044	0.14	
				10.7	1.0093	1.0601				9.2	1.017	0.9046			
				10.3	1.0064	1.0234				9.4	1.009	0.9316			
				10.9	1.0225	1.0660				8.7	1.064	0.8177			
				10.2	1.0194	1.0006				9.7	1.093	0.8875			
				10.3	1.0079	1.0219				9.3	1.014	0.9172			
				9.7	1.0124	0.9581				9.4	1.027	0.9153			
5100C	10.0	0.10	0.0587	9.6	1.0128	0.9479	0.0308	0.097	0.0550	7.3	1.165	0.6266	0.128	0.40	
				9.7	1.0093	0.9611				8.3	1.017	0.8161			
				9.2	1.0064	0.9141				8.1	1.009	0.8028			
				8.9	1.0225	0.8704				6.6	1.064	0.6203			
				9.1	1.0194	0.8927				7.7	1.093	0.7045			
				9.2	1.0079	0.9128				8.8	1.014	0.8679			
				9.3	1.0124	0.9186				9.9	1.027	0.9640			
4100	10.0	0.10	0.0000	10.0	1.0128	0.9874	0.0515	0.162	0.0000	10.8	1.165	0.9270	0.045	0.14	
				10.1	1.0093	1.0007				8.4	1.017	0.8260			
				9.0	1.0064	0.8943				9.4	1.009	0.9316			
				9.4	1.0225	0.9193				9.5	1.064	0.8929			
				9.5	1.0194	0.9319				9.8	1.093	0.8966			
				10.0	1.0079	0.9922				9.7	1.014	0.9566			
				10.5	1.0124	1.0371				9.8	1.027	0.9542			

Reference: 40 CFR 136, Appendix B (ERA Inorganic Blank Sand & AEC Standard Soil)/SW846

GMDLSOIL

VANADIUM BY GFAA
(USAEC METHOD GV1)

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **ANALYSIS OF AQUEOUS SAMPLES FOR VANADIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7911)
USAEC METHOD - GV1 - WATER**

TABLE OF CONTENTS

TITLE: **ANALYSIS OF AQUEOUS SAMPLES FOR VANADIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3020/7911) USAEC METHOD - GV1 - WATER**

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental aqueous samples and wastes with suspended solids for vanadium (V) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Aqueous samples for GFAAS determination of vanadium are digested by EPA SW-846 Method 3020 and analyzed by EPA SW-846 Method 7841.

1.2.2 The only deviations to these methods is the initial and final volume of sample digested is 50 mL instead of 100 mL.

1.2.3 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at approximately twice the reporting limit and two spikes at approximately twenty times the reporting limit will be digested and analyzed with each lot of samples.

1.2.4 A representative 50 mL aliquot of sample is prepared for analysis by refluxing on a hot plate with nitric acid in a covered beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. The digestate is then cooled, filtered and diluted to 50 mL.

1.2.5 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of light at a specific wavelength during atomization is measured and the concentration of vanadium in the sample is calculated based on the instrument's calibration curve. Element specific instrument conditions are listed in section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annual and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for vanadium in aqueous samples are reported below:

Element	MDL (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)
Vanadium	5.0	5.0	200

1.4. INTERFERENCES

1.4.1 Vanadium is refractory and prone to form carbides. Pyrolytically coated graphite tubes are used to minimize the formation of carbides and to increase sensitivity.

1.4.2 Laboratory control samples are used to verfify that the digestion procedure was appropriate.

1.4.3 A matrix modifier is added to the sample to minimize volatilization losses during the drying and ashing steps of the graphite furnace temperature program and to minimize matrix interferences (the Perkin-Elmer Model 4100ZL does not routinely require the use of a matrix modifier).

1.4.4 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.4.5 Nitrogen should not be used as a purge gas.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of aqueous samples with nitric acid which is corrosive. Adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain nitric acid, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;

2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;

2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;

2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);

2.1.5 Disposable beakers, 10-mL capacity;

2.1.6 Class A volumetric flasks (1000 mL, 200 mL, 100 mL);

2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);

2.1.8 Graduated cylinders (50 mL);

2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;

2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer instrument equipped with a Model HGA-600 graphite furnace, Zeeman background correction, a hollow cathode lamp (HCL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube;

2.2.2 Purge gas - Argon, 99.9% pure;

2.2.3 Matrix modifier (5100Z) - 500 ppm palladium nitrate;

2.2.4 Matrix modifier (4100ZL) - none;

2.2.5 Sample injection volume - 20 uL;

2.2.6 Matrix modifier injection volume (5100Z) - 5 uL;

2.2.7 Duplicate burns for all standards and samples with the average reported as the final result;

2.2.8 Wavelength - 318.4 nanometers (nm);

2.2.9 Slitwidth - 0.7 nm.

2.2.10 Vanadium furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	5-10	20-60
	2	1100-1600	10-30	20-60
	3	2500	0-5	3-10
	4	2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	1100-1600	10-30	20-60
	3	2650	0-5	3-10
	4	2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).

Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.

Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.

Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.

Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.

2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.

2.3.3 Nitric acid (1+1) - using a 100 mL graduated cylinder, 100 mL of conc. HNO_3 is added to 100 mL deionized water and placed in a nalgene dispenser bottle.

2.3.4 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.5 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 V standard solution: Use a commercially purchased 1,000 milligram-per-liter (mg/L) stock solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Vanadium Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L vanadium stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 200 μg/L Vanadium Standard (C2): Using a volumetric pipet, 2.0 mL of the 10 mg/L vanadium intermediate (C1) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 μg/L Vanadium Standard (C3): Using a volumetric pipet, 5 mL of the 200 μg/L vanadium standard (C2) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 200 μg/L and 10 μg/L vanadium standards with a 5% HNO_3 solution (see Sec. 3.1).

2.4.6 5 mg/L Vanadium Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L vanadium stock is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NIST reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 100 ug/L V continuing calibration verification solution (CCV): using a volumetric pipet transfer 2.0 mL of the 10 mg/L vanadium intermediate (C1) is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 5-percent HNO_3 solution: using a Nalgene dispenser bottle, 5 mL conc. HNO_3 is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for V is 7740-62-2, its atomic weight is 50.94 and density 5.8 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

200 ug/L and 10 ug/L vanadium standards are prepared as outlined in Sec. 2.4. Additional calibration standards for V are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Vanadium

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	200	20	0	200
C2	200	10	10	100
C2	200	5	15	50
C3	10	20	0	10
C3	10	10	10	5
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for V by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 200 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (100 ug/L V) is reanalyzed. If the measured concentration for this standard is not $\pm$ 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Aqueous samples for metals analysis must be preserved with nitric acid to a pH of less than 2. The pH of the sample should be checked after addition to the container to insure that the pH is less than or equal to 2, and more acid added if necessary.

4.2 SAMPLING CONTAINERS

Aqueous samples are taken in one liter polypropylene bottles with screw caps.

4.3 STORAGE CONDITIONS

Samples are shipped to and stored in the laboratory at room temperature.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 PROCEDURE

5.1. SAMPLE DIGESTION

5.1.1 Using a graduated cylinder, transfer a 50 mL aliquot of well-mixed sample to a 150 mL beaker or erlenmeyer flask. Add 1.5 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 1.5 mL portion of concentrated HNO_3. Cover the beaker with a non-ribbed watch glass, return to the hot plate and gently reflux.

5.1.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL) using a ribbed watch glass and not allowing any portion of the bottom of the beaker to do dry. Remove the beaker and add approximately 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

5.1.3 Remove the beaker and allow to cool. Wash down the beaker walls with Type I water and filter, if necessary. Filtration should be done only if there is concern that insoluble material may clog the autosampler. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute HNO_3 prior to use.

5.1.4 Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 5% (v/v) HNO_3.

5.1.5 Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.6 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.7 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.8 Enter the digestion date in the computer.

5.1.9 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7911 (1986).

5.2.5 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported vanadium concentration for that sample should be qualified as having a possible interference.

5.2.6 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.7 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.8 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within $\pm$ 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.9 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.10 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.11 When MSA is required, four 5.0 mL aliquots of sample are spiked with 0, 20, 40, and 60 uL respectively of a 5.0 mg/L V solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (cc) for each set. If the cc is less than 0.995, repeat the analysis once. If the cc is still less than 0.995, the original sample response will be reported and qualified as having a possible interference.

5.2.12 Attachment 3 shows a typical GFAA run sequence.

6.0 CALCULATIONS

6.1 The Perkin-Elmer 5100Z and 4100ZL instruments determine the absorbance-seconds of V in the sample digestate and calculate the sample concentration in ug/L directly from the standard curve. If the sample concentration of V is within the calibration range, the sample concentration will be reported as as calculated by the instrument. If the concentration of V is either not detected or below the method detection limit, the sample concentration will be reported as less than the method detection limit. If the concentration of V is greater than the highest calibration standard, the sample digestate should be diluted within range and reanalyzed. The concentration in the diluted sample and the dilution factor are reported. The highest calibration range for V is 200 ug/L as given in Sec. 1.3. When MSA is performed, the result from this analysis will be used unless the cc <0.995.

6.2 Post digestion spikes (SPX) are prepared by adding one part high standard (200 ug/L) to one part sample. A dilution factor of two is entered in the data batch and the target concentration will equal the concentration of the high standard (200 ug/L).

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, 1.0 mL of 1000 ppm stock standard that is commercially purchased is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 1000 ug-V/L. This solution is prepared fresh monthly (see Section 2.4.10 for policy on stock standard source).

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 50 mL of deionized water:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)
Blank	--	0
Low	0.5	10
High	5.0	100
High	5.0	100

7.1.3 When required, sample matrix spikes are prepared by adding 5.0 mL of the spike solution to 2-50 mL aliquots of the sample. The target concentration will be 100 ug/L.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.

2. Difference between the two high concentration spiked QC samples in each lot.

3. Three-point moving average percent recovery for the low level spike in each lot.

4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.5 EPA Method 7911 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.6 EPA Method 3020 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

October 27, 1993

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (Pb, Tl, & V)	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of Pb & Tl 1000 ppm stock standards and 1.0 mL of V 1000 ppm stock standard are transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for Pb & Tl and 1000 ug/L for V. This solution is prepared fresh monthly.

2. Prepare quality control samples:
   a. Method blank (MB) - reagents only.
   b. Low spike (SP1) - add 0.5 mL of spike solution to 50 mL DI.
   c. High spike (SP2, SP3)- add 5.0 mL of spike solution to 2-50 mL aliquots of DI.
   d. Sample matrix spikes (SPM1, SPM2)- add 5.0 mL of spike solution to 2-50 mL aliquots of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
Pb, Tl	5 ug/L	50 ug/L	50 ug/L
V	10 ug/L	100 ug/L	100 ug/L

DIGESTION PROCEDURE:

1. Using a graduated cylinder, transfer a 50 mL aliquot of sample to a 150 mL beaker or erlenmeyer flask. Add 1.5 mL of conc HNO_3. Cover with a ribbed watch glass. Place on a hot plate and cautiously evaporate to a low volume (5 mL) making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool and add another 1.5 mL portion of conc. HNO_3. Cover with a non-ribbed watch glass, return to the hot plate and gently reflux.

2. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL) using a ribbed watch glass and not allowing any portion of the bottom of the beaker to do dry. Remove the beaker and add approx. 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

3. Remove and cool. Wash down the beaker walls with Type I water and filter, if necessary.

4. Adjust the final volume to 50 mL with Type I water. The digested samples will have an approximate acid concentration of 5% (v/v) HNO_3.

5. Record the prep in ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number, and expiration dates). Place a copy of the logbook page in the box with the digestates.

6. Enter the digestion date in the computer.

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (Pb, Tl & V)	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.

2. Prepare the following standards for instrument dilution (Note: standards should be 5% HNO_3):

Element	Conc.(ug/L)	Calibration Curves (ug/L)
Pb	100 & 10	100, 50, 25, 10, 2.0, 0.0
Tl	100 & 10	100, 50, 25, 10, 2.5, 0.0
V	200 & 10	200, 100, 50, 10, 5.0, 0.0

3. Method detection limits (MDL):
   Pb = 2.0 ug/L Tl = 2.5 ug/L V = 5.0 ug/L
4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.

5. Analyze the standard curve. The cc must be > 0.995.

6. Analyze the ICV. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

7. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.

8. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD is greater than 20% for a sample whose concentration exceeds twice the MDL, reanalyze the sample. If RPD is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.

9. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

10. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within $\pm$ 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

11. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not $\pm$ 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L MSA solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.s:	Aqueous Samples by GFAA (Pb, Tl & V)	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS (Chemical Laboratory Analysis and Scheduling System) data batch. CLASS is ESE's computerized data management system.

2. If the method blank has a response greater than the instrument detection limit the data must be reviewed by the department manager to determine is the data is acceptable.

3. If the method blank (or any sample with a SPM or SPX) has a response less than the instrument detection limit, enter the response as 0 Final so that CLASS will not use the response in the recovery calculations.

4. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.

5. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 - TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank	
Standard 1 (2.5 ug/L)	
Standard 2 (10.0 ug/L)	
Standard 3 (25.0 ug/L)	
Standard 4 (50.0 ug/L)	
Standard 5 (100 ug/L)	
Initial calibration verification - ICV (reference)	± 10%
Method blank (MB)	
Low spike (SP1)	see control charts
High spike (SP2)	see control charts
High spike (SP3)	see control charts
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike dup	
Sample #2	
CCV (50 ug/L)	± 10%
Continuing calibration blank - CCB	
Sample #3 through #12	
CCV (50 ug/L)	± 10%
CCB	
Sample #13 through #20	
Serial Dilution (1+4)	± 10%
or Post-Digestion Spike (SPX)	± 15%
CCV (50 ug/L)	± 10%
CCB	
MSA - 0	
MSA - 1	
MSA - 2	
MSA - 3	
CCV (50 ug/L)	± 10%
CCB	

ATTACHMENT 3.0 - MDL STUDY

October 27, 1993

GFAA Instrument & Method Detection Limits
JANUARY 1993

Element	Spike Conc. (ug/L)	Day 1 Response (ug/L)	Day 1 SD (ug/L)	Day 2 Response (ug/L)	Day 2 SD (ug/L)	Day 3 Response (ug/L)	Day 3 SD (ug/L)	IDL (ug/L)	Combined Reported IDL (ug/L)	Unspiked Response (ug/L)	Spiked Response (ug/L)	MDL (ug/L)	Combined Reported MDL (ug/L)
Vanadium	10.0									0.9	10.9	3.5	5.0
5100A											8.7		
											10.1		
											11.3		
											10.0		
											11.4		
											8.8		
5100B	10.0									1.5	11.0	1.3	
											10.4		
											10.6		
											10.3		
											10.6		
											10.3		
											11.4		
5100C	10.0									0.5	9.0	2.2	
											8.5		
											7.9		
											10.0		
											9.6		
											9.1		
											8.5		
4100	10.0									0.0	7.2	4.6	
											8.0		
											6.5		
											6.9		
											6.8		
											5.7		
											10.3		

Reference: CLP390 (ILM01.0) & 40 CFR 136, App. B/SW846

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **ANALYSIS OF SOIL AND SEDIMENT SAMPLES FOR VANADIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3050/7911) USAEC METHOD - GV1 - SOIL**

TABLE OF CONTENTS

TITLE: **ANALYSIS OF SOIL AND SEDIMENT SAMPLES FOR VANADIUM BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY (SW-846 METHOD 3050/7911) USAEC METHOD - <u>GV1</u> - SOIL**

1.0 SUMMARY/APPLICATION

1.1 ANALYTES

This method is applicable for the analysis of all environmental soil and sediment samples for vanadium (V) by graphite furnace atomic absorption spectroscopy (GFAAS) for U.S. Army Environmental Center (USAEC) projects. This method is designed to provide the lowest reporting limit that is consistent with routine analytical procedures.

1.2 GENERAL METHOD

1.2.1 Soil and sediment samples for GFAAS determination are digested by EPA SW-846 Method 3050 and analyzed following EPA SW-846 Method 7911. The are no deviations from these methods.

1.2.2 Additional quality control requirements applicable for the Class I analysis of samples under the USAEC guidelines for implementation of ER 1110-1-263 have been added. A daily control spike at twice the reporting limit and two spikes at twenty times the reporting limit will be digested and analyzed with each lot of samples.

1.2.3 A representative 1-2 g (wet weight) sample is prepared for analysis by refluxing on a hot plate at approximately 95°C with a mixture of nitric acid and hydrogen peroxide in a covered beaker. The digestate is then cooled, filtered and diluted to 100 mL.

1.2.4 Representative aliquots of the final digestate and an aliquot of matrix modifier are placed by means of an automatic sampler, into a graphite furnace atomic absorption spectrophotometer for analysis. Each aliquot is evaporated to dryness, charred (ashed) and atomized. The absorption of light at a specific wavelength during atomization is measured and the concentration of vanadium in the sample is calculated based on the instrument's calibration curve. Element specific instrument conditions are listed in section 2.2.

1.3 REPORTING LIMITS, LOWER AND UPPER STANDARD RANGE

1.3.1 Method detection limits (MDL) are determined annual and verified quarterly and after any major maintenance or modifications to the instrument. MDLs are calcualted by the procedure outlined in 40CFR136, Appendix B.

1.3.2 The method detection limit and lower and upper standard range for vanadium in soil and sediment samples are reported below:

Element	MDL (ug/g)	Lower Standard Range (ug/g)+	Upper Standard Range (ug/g)+
Vanadium	0.75	0.5	20.0

+ Based on 1 g of soil and 100 mL final volume

1.4. INTERFERENCES

1.4.1 Vanadium is refractory and prone to form carbides. Pyrolytically coated graphite tubes are used to minimize the formation of carbides and to increase sensitivity.

1.4.2 Laboratory control samples are used to verify that the digestion procedure was appropriate.

1.4.3 A matrix modifier is added to the sample to minimize volatilization losses during the drying and ashing steps of the graphite furnace temperature program and to minimize matrix interferences.

1.4.4 Zeeman background correction is used to avoid erroneous results that may be due to nonwavelength-specific absorption and light scattering during atomization. A "clean-out" step is included in the furnace program to prevent memory effects due to incompletely volatilized samples.

1.4.5 Nitrogen should not be used as a purge gas.

1.5. ANALYSIS RATE

After instrument calibration, one analyst can analyze approximately 20 samples in an 8-hour day. Approximately 20 samples can be digested in an 8-hour day.

1.6. SAFETY INFORMATION

This method involves digestion of soil and sediment samples with a mixture of nitric acid and 30 percent hydrogen peroxide. Both of these reagents are corrosive, and adequate dermal and eye protection are required. Sample digestions should only be carried out in a hood with adequate ventilation. Standards are both toxic and, since they contain nitric acid, also corrosive. The instrument should be adequately ventilated.

2.0 APPARATUS AND CHEMICALS

2.1. GLASSWARE/HARDWARE

2.1.1 Analytical balance, capable of weighing accurately to 0.0001 g;

2.1.2 Heavy duty beakers, 150 mL with watchglass covers or 125 erlenmeyer flasks with covers;

2.1.3 Hot plate, adjustable and capable of maintaining a temperature of 95°C;

2.1.4 Adjustable Eppendorf pipet, with disposable tips (1000 uL);

2.1.5 Disposable beakers, 10-mL capacity;

2.1.6 Class A volumetric flasks (1000 mL, 200 mL, 100 mL);

2.1.7 Class A volumetric pipets (10mL, 5 mL, 2 mL);

2.1.8 Graduated cylinders (100 mL);

2.1.9 Filtering apparatus and glass-fiber filters, Gelman-47 millimeters (mm) or equivalent;

2.1.10 Nalgene dispenser bottle (500-mL).

2.2. INSTRUMENTATION

Perkin-Elmer Model 5100Z, or 4100ZL Atomic Absorption Spectrophotometer instrument equipped with a Model HGA-600 graphite furnace, Zeeman background correction, a hollow cathode lamp (HCL) and with the conditions optimized as outlined below:

2.2.1 Pyrolytic graphite tube;

2.2.2 Purge gas - Argon, 99.9% pure;

2.2.3 Matrix modifier (5100Z) - 500 ppm palladium nitrate;

2.2.4 Matrix modifier (4100ZL) - none;

2.2.5 Sample injection volume - 20 uL;

2.2.6 Matrix modifier injection volume (5100Z) - 5 uL;

2.2.7 Duplicate burns for all standards and samples with the average reported as the final result;

2.2.8 Wavelength - 318.4 nanometers (nm);

2.2.9 Slitwidth - 0.7 nm.

2.2.10 Vanadium furnace program (approximate settings):

Instrument	Step No.	Temp (°C)	Ramp (sec)	Hold (sec.)
PE-4100	1	120-150	5-10	20-60
	2	1100-1600	10-30	20-60
	3	2500	0-5	3-10
	4	2650	1	5
PE-5100	1	120-150	5-20	20-60
	2	1100-1400	10-30	20-60
	3	2650	0-5	3-10
	4	2650	1	5

Variables under the analyst's control are the heating parameters for the graphite furnace temperature program. Some samples can be analyzed using the manufacturer's Recommended Conditions, however, with complex samples containing unknown compositions, alterations to the temperature program are necessary to achieve optimum performance. Method development is typically performed by the group leader or a lead analyst and the program is stored in the instrument computer for future use. A typical furnace temperature program will include the following steps:

Drying step - after the sample is deposited in the furnace, it must be dried at a sufficiently low temperature to avoid splattering. Temperatures around 80 - 150 degrees Celsius (°C) are common. Use of a temperature "ramp" provides a variable time over which the temperature is increased. The temperature is then held until drying is complete - typically less than one minute. The internal gas flow is normally left at the default value of 300 milliliters per minute (mL/min).

Thermal Pretreatment (pyrolysis or char step) - is used to remove as much of the matrix as possible before atomization. The maximum temperature for thermal pretreatment will depend on the analyte and the matrix. Ramp and hold times will also be determined by the matrix components. The internal gas flow is normally set at 300 mL/min. This step is often not required for the 4100ZL.

Optional Pre-atomization Cool-down step - is used to maximize the heating rate and extend the isothermal zone within the graphite tube during atomization. This results in improved sensitivity and reduced peak tailing for a number of elements. The cool-down step is usually at 20 °C with a flow rate of 300 mL/min.

Atomization step - a fast heating rate and the lowest possible atomization temperature are normally selected to extend the lifetime of the graphite tube. However, the temperature selected must be high enough to guarantee complete volatilization of the analyte within a few seconds. The internal gas flow is reduced or stopped during the atomization step to increase the residence time of the atomic vapor in the furnace. The read function is activated at the beginning of the atomization step.

Clean-out and Cool-down steps - after atomization, the graphite furnace may be heated to a higher temperature (up to 2650 °C) to burn off any sample residue which may remain in the furnace. A preset cool down step is automatically included in each furnace cycle to return the furnace to 20 °C prior to the injection of the next sample. Flow rates for both steps are at 300 mL/min.

2.3 REAGENTS

2.3.1 American Society for Testing Materials (ASTM) Type I grade deionized water.

2.3.2 Concentrated nitric acid (HNO_3), trace metals grade.

2.3.3 Hydrogen Peroxide (H_2O_2) - 30 percent, trace metals grade.

2.3.4 Nitric acid (1+1) - using a 100 mL graduated cylinder, 100 mL of conc. HNO_3 is added to 100 mL deionized water and placed in a nalgene dispenser bottle.

2.3.5 Palladium nitrate stock solution, 10,000 ppm Pd: purchased from Perkin-Elmer or equivalent.

2.3.6 500 ppm $Pd(NO_3)_2$ modifier: 5.0 mL of the 10,000 ppm $Pd(NO_3)_2$ stock solution is diluted to 100 mL with deionized water in 100 mL volumetric flask.

2.3.7 USAEC Standard Soil.

2.4 SARMS, CALIBRATION AND CHECK SOLUTIONS

2.4.1 V standard solution: Use a commercially purchased 1,000 milligram-per-liter (mg/L) stock solution. Standard solutions must be traceable to NIST standard reference material. Certificates of analysis are required for all stock solutions purchased and are kept on file in the purchasing department.

2.4.2 10 mg/L Vanadium Intermediate solution (C1): Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L Vanadium stock is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.3 200 μg/L Vanadium Standard (C2): Using a volumetric pipet, 2.0 mL of the 10 mg/L vanadium intermediate (C1) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.4 10.0 μg/L Vanadium Standard (C3): Using a volumetric pipet, 5 mL of the 200 μg/L vanadium standard (C2) is transferred to a 100 mL volumetric flask, 5 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared fresh, daily.

2.4.5 The instrument autosampler will prepare additional calibration standards by diluting the 200 μg/L and 10 μg/L vanadium standards with a 5% HNO_3 solution (see Sec. 3.1).

2.4.6 5 mg/L Vanadium Method of Standard Addition (MSA) spiking solution: Using a calibrated Eppendorf pipet, 1.0 mL of the 1000 mg/L vanadium stock is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution expires 33 days after the preparation date.

2.4.7 The initial calibration verification solution (ICV) is an independent standard, prepared from different stock solutions than those used to prepare the calibration standards. Typically an EPA or NIST reference is used for the ICV and is prepared according to the supplier's instructions.

2.4.8 100 ug/L V continuing calibration verification solution (CCV): using a volumetric pipet transfer 2.0 mL of the 10 mg/L vanadium intermediate (C1) is transferred to a 200 mL volumetric flask, 10 mL conc. HNO_3 added and then diluted to volume with Type I water. This solution is prepared daily.

2.4.9 The continuing calibration blank (CCB) is a 5-percent HNO_3 solution: using a Nalgene dispenser bottle, 5 mL conc. HNO_3 is transferred to a 100 mL volumetric flask and then diluted to volume with Type I water. This solution is also used by the instrument to make dilutions.

2.4.10 All standard and check solutions should have an acid concentration of 5% (v/v) HNO_3. In addition, different stock solutions should be used for preparation of the calibration standards, ICV and the digestion spike solutions. If an alternate source is not available, these solutions should be prepared on a different day and/or by a different analyst. These solutions should be stored at ambient temperature in the laboratory.

2.4.11 All standards and check solution preparations are recorded in the ESE Standard Prep Logbook and include the manufacturer, lot number, date received and expiration date.

2.5 ANALYTES

The Chemical Abstract Service (CAS) Registry Number for V is 7740-62-2, its atomic weight is 50.94 and density 5.8 g/cc.

3.0 CALIBRATION

3.1 PREPARATION OF CALIBRATION STANDARDS

200 ug/L and 10 ug/L vanadium standards are prepared as outlined in Sec. 2.4. Additional calibration standards for V are prepared by the instrument autosampler as outlined below:

Working Calibration Standards Preparation for Vanadium

Standard Used	Concentration of Standard Used (ug/L)	Volume of Standard Used (uL)	Volume of 5-Percent HNO3 (uL)	Concentration of Prepared Standard (ug/L)
C2	200	20	0	200
C2	200	10	10	100
C2	200	5	15	50
C3	10	20	0	10
C3	10	10	10	5
-	-	-	20	0

3.2 INITIAL CALIBRATION

The instrument is optimized according to manufacturers instructions with the conditions described in Sec. 2.2 with a minimum of five standards which include a blank, a standard at the lower reporting limit and a standard at the upper reporting limit. The calibration standards listed in Sec. 3.1 are analyzed. The instrument will construct a standard curve for V by plotting absorbance-seconds versus the concentration (ug/L) of the calibration standards. The correlation coefficient for the standard curve must be 0.995 or greater.

3.2.1 Duplicate burns are required for each standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a standard, the analysis of that standard should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the instrument conditions should be optimized again and calibration repeated.

3.2.2 Calibration Checks - After calibration the ICV solution is analyzed. If the measured concentration is not within 10% of the true value, the 200 ug/L and 10 ug/L standards are prepared again and/or the instrument recalibrated. In addition, after every ten samples and at the end of each day's analysis the CCV solution (100 ug/L V) is reanalyzed. If the measured concentration for this standard is not ± 10% of the true value, the instrument is recalibrated and all samples since the last acceptable CCV are reanalyzed.

3.3. DAILY CALIBRATION

Daily calibration will be performed as stated in Sec. 3.2.

4.0. SAMPLE HANDLING AND STORAGE

4.1 SAMPLING PROCEDURE AND PRESERVATION

Soil and sediment samples for metals analysis must be maintained in a temperature-controlled room at 4 degrees Celsius (°C).

4.2 SAMPLING CONTAINERS

Environmental soil and sediment samples are collected in wide-mouth, amber-glass jars with teflon-lined lids.

4.3 STORAGE CONDITIONS

Samples are shipped and stored in the laboratory at 4° C.

4.4 HOLDING TIME LIMITS

The holding time between sampling and completion of analysis is six months.

4.5 SOLUTION VERIFICATION

Verification of the calibration standards is based on the analysis of daily QC spikes and analysis of independently prepared reference standards. After preparation, the spike solution is analyzed by the ICP prior to use in the daily control spikes.

5.0 <u>PROCEDURE</u>

5.1. SAMPLE DIGESTION

5.1.1 Mix the sample thoroughly to achieve homogeneity. Weigh directly into a beaker or erlenmeyer flask, a 1 to 2 g aliquot of sample to the nearest 0.0001 g. For samples with low percent solids a larger sample size may be necessary.

5.1.2 Add 10 mL of 1+1 HNO_3 and mix the slurry. The sample is covered with a non-ribbed watch glass and refluxed on a hot plate at 95°C for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.

5.1.3 Allow the sample to cool and add 2 mL Type I water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool.

5.1.4 Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or until the general sample appearance is unchanged. Do not add more than a total 10 mL of 30% H_2O_2.

5.1.5 Cover the beaker with a ribbed watch glass and continue heating until the volume has been reduced to approximately 5 mL. Remove the beaker and allow the sample to cool. Wash down the beaker walls with Type I water and filter or centrifuge the sample to remove particulates that could clog the GFAA autosampler during analyses. The filter and filtering apparatus are thoroughly cleaned and pre-rinsed with dilute nitric acid prior to use.

5.1.6 Adjust the final volume to 100 mL with Type I water. The digested sample will have an approximate acid concentration of 5% (v/v) HNO_3.

5.1.7 A reagent blank should also be carried through the entire digestion procedure.

5.1.8 A method blank, one low-level spike and two high-level spikes are also digested with the samples. See Sec. 7.0. for preparation of the daily QC samples.

5.1.9 Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.

5.1.10 Enter the digestion date and sample weights in the computer.

5.1.11 The samples are now ready for analysis as described in Sec. 5.2.

5.2. INSTRUMENTAL ANALYSIS

5.2.1 Daily instrument calibration is performed as described in 3.2.

5.2.2 Analyze the standard curve. If the correlation coefficient for the standard curve is not 0.995 or greater, the curve must be reanalyzed. If the correlation coefficient is acceptable, print the standard curve and continue the analysis.

5.2.3 Analyze an initial calibration verification solution (ICV) after the standard curve. If the ICV is not within ± 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.

5.2.4 Analyze the reagent blank. If the reagent blank is greater than twice the method detection limit, the samples must be redigested and the newly prepared samples analyzed or an adequate explanation provided as to why the original samples should be acceptable.

5.2.5 Analyze the method blank, low-level spike, high-level spikes and samples according to EPA SW846 Method 7911 (1986).

5.2.6 Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the relative percent difference (RPD) between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, the analysis of that sample should be repeated. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported vanadium concentration for that sample should be qualified as having a possible interference.

5.2.7 If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.

5.2.8 A sample matrix spike and matrix spike duplicate, when required, will be digested and analyzed at a frequency of 5%. If the spike recovery does not fall within 20% of the true value, a matrix interference should be suspected.

5.2.9 A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within $\pm$ 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.

5.2.10 Interference tests: For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.11 If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, a matrix interference should be suspected and MSA performed on all samples in the batch.

5.2.12 When MSA is required, four 5.0 mL aliquots of sample are spiked with 0, 20, 40, and 60 uL respectively of a 5.0 mg/L V solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (cc) for each set. If the cc is less than 0.995, repeat the analysis once. If the cc is still less than 0.995, the original sample response will be reported and qualified as having a possible interference.

5.2.13 Attachment 3 shows a typical GFAA run sequence.

6.0 CALCULATIONS

6.1 The Perkin-Elmer 5100Z and 4100ZL instruments determine the absorbance-seconds of V in the sample digestate and calculate the sample concentration in ug/L directly from the standard curve. If the sample concentration of V is within the calibration range, the sample concentration will be reported as calculated from Sec.6.2. If the concentration of V is either not detected or below the method detection limit, the sample concentration will be reported as less than the method detection limit. If the concentration of V is greater than the highest calibration standard, the sample digestate should be diluted within range and reanalyzed. The concentration in the diluted sample and the dilution

factor are reported. The highest calibration range for V is 20.0 ug/g (200 ug/L) as given in Sec. 1.3. When MSA is performed, the result from this analysis will be used unless the cc <0.995.

6.2 For soils and sediments, the measured ug/L concentration or MSA value, digested sample weight and percent solids are entered in the data batch. If a dilution was required, the concentration in the diluted sample and the dilution factor are entered in the data batch. Dry weight results are based on the following calculation:

$$\text{Conc, dry (ug/g)} = \frac{\text{Conc. in digestate (ug/L) x Digestate vol. (L)}}{\text{Wet weight of sample (g) x \% solids}}$$

6.3 Post digestion spikes (SPX) are prepared by adding one part high standard (200 ug/L) to one part sample. A dilution factor of two is entered in the data batch and the target concentration will equal the concentration of the high standard (200 ug/L).

7.0 DAILY QUALITY CONTROL

7.1 PREPARATION OF DAILY CONTROL SAMPLES

7.1.1 AEC spike solution: using a volumetric pipet, 1.0 mL of 1000 ppm stock standard that is commercially purchased is transferred to a 1-L volumetric flask containing deionized water and 10 mL conc. HNO_3 and then diluted to volume with deionized water. The final concentration will be 1000 ug-V/L. This solution is prepared fresh monthly (see Section 2.4.10 for policy on stock standard source).

7.1.2 Daily control spike samples are prepared by adding the following volumes of spike solution to 0.1 g of standard soil:

Daily Control Spike	Volume of Spike Solution Used (mL)	Conc. of Control Spike (ug/L)	Conc. of Control Spike (ug/g)+
Blank	--	0	0
Low	1.0	10	1.0
High	10.0	100	10.0
High	10.0	100	10.0

+Note: ug/g target concentrations for control spikes are based on 1.0 g. The actual weight of standard soil used is multiplied by 10 per USAEC instructions.

7.1.3 When required, sample matrix spikes are prepared by adding 10.0 mL of the spike solution to 2-1.0 g portions of the sample. The target concentration will be 10.0 ug/g.

7.1.4 Each control spike and sample matrix spike is digested and analyzed as described in Sec. 5.0 .

7.2. CONTROL CHARTS

Control charts are prepared using the percent recovery data from both the duplicate high level spikes and the low level spike calculated according to the following equation:

$$\% \text{ Recovery} = \frac{\text{Found Conc.}}{\text{Spiked Concentration}} \times 100 \text{ percent}$$

Preparation of control charts requires the following data:

1. Average percent recovery of the two high concentration spiked QC samples in each lot.
2. Difference between the two high concentration spiked QC samples in each lot.
3. Three-point moving average percent recovery for the low level spike in each lot.
4. Three-point moving average difference for the low concentration spike.

For values that fall outside the control limits and data points that are deemed as outliers, the data will be evaluated and corrective action will be taken.

8.0 REFERENCES

8.1 U.S. Army Environmental Center Guidelines for Implementation of ER 1110-1-263 for USAEC Projeccts, May 1992.

8.2 Occupational Safety and Health Administration, OSHA 2206, "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), (Revised, January 1976).

8.3 Federal Register, Vol. 40, No. 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," July 1, 1990.

8.4 EPA Method 3050 - Test Methods for Evaluating Solid Wastes, EPA SW 846, 3rd Edition, September 1986.

8.5 EPA Method 7000 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

8.6 EPA Method 7911 - Test Methods for Evaluating Solid Wastes, EPA SW 846 3rd Edition, September 1986.

9.0 ATTACHMENTS

1.0 Method Summary

2.0 Typical GFAA Run Sequence

3.0 MDL Study

ATTACHMENT 1.0 - METHOD SUMMARY

Lot No.:________

SUMMARY OF METHOD

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

PREPARATION OF DAILY CONTROL SPIKE SAMPLES

1. AEC spike solution: using a calibrated eppendorf pipet, 0.5 mL of As, Se, & Tl 1000 ppm stock standards 0.8 mL of Pb 1000 ppm stock standard, and 1.0 mL of V 1000 ppm stock standard are transferred to a 1-L volumetric flask containing deionized water and 10 mL of conc. HNO_3 and then diluted to volume with deionized water. The final concentration for the spike solution will be 500 ug/L for As, Se, & Tl, 800 ug/L for Pb and 1000 ug/L for V. This solution is prepared fresh monthly.
2. Prepare quality control samples:
   a. Reagent blank - reagents only.
   b. Method blank (MB) - 0.1 g portion of standard soil plus reagents.
   c. Low spike (SP1) - add 1.0 mL of spike solution to 0.1 g portion of standard soil.
   d. High spike (SP2,SP3)- add 10.0 mL of spike solution to 2-0.1 g portions of standard soil.
   e. Sample matrix spikes (SPM1, SPM2)- add 10.0 mL of spike solution to 2-1.0 g portions of sample.

Analyte	Low Spike Target	High Spike Target	Sample Spike Target
As, Se, Tl	0.5 ug/g (5 ug/L)	5.0 ug/g (50 ug/L)	5.0 ug/g (50 ug/L)
Pb	0.8 ug/g (8 ug/L)	8.0 ug/g (80 ug/L)	8.0 ug/g (80 ug/L)
V	1.0 ug/g (10 ug/L)	10.0 ug/g (100 ug/L)	10.0 ug/g (100 ug/L)

Note: ug/g target concentrations for low and high spike are based on 1.0 g.

DIGESTION PROCEDURE:

1. Mix the sample thoroughly. Weigh into a beaker or erlenmeyer flask, a 1-2 g aliquot of sample to the nearest 0.0001 g. For samples with low % solids a larger sample size may be necessary.
2. Add 10 mL of 1+1 HNO_3 and mix. Cover with a non-ribbed watch glass and reflux on a hot plate at 95°C for 10-15 minutes without boiling. Cool the sample, and add 5 mL conc. HNO_3, replace the watch glass and reflux for 30 minutes. Add another 5 mL conc. HNO_3 and evaporate to 5 mL without boiling. Maintain a covering of solution over the bottom of the beaker.
3. Allow the sample to cool. Add 2 mL Type I water and 3 mL 30% H_2O_2. Cover with a watch glass and return the beaker to the hot plate. Remove the beaker if the effervescence becomes too vigorous to avoid loss of sample. Heat until the effervescence subsides and allow the beaker to cool. Continue to add 30% H_2O_2 in 1 mL aliquots while warming until the effervescence is minimal or the general appearance is unchanged. Do not add more than a total 10 mL of H_2O_2.
4. Cover with a ribbed watch glass and continue heating until the volume has been reduced to approx. 5 mL. Remove the beaker and allow to cool. Wash down the beaker walls with deionized water and filter if necessary. Adjust the final volume to 100 mL with Type II water. The digested sample will have an approximate acid concentration of 5% (v/v) HNO_3.
5. Record the prep in the ESE prep logbook. Include the SOP number and any reagents used (with the manufacturer, lot number and expiration dates). Place a copy of the logbook page in the box with the digestates.
6. Enter the digestion date and sample weights in the computer.

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

INSTRUMENT ANALYSIS:

1. Instrument: Perkin-Elmer 5100Z or 4100ZL Spectrophotometer.
2. Prepare the following standards for instrument dilution (Note: standards should be 5% HNO_3):

Element	Conc.(ug/L)	Calibration Curves (ug/L)
As,Pb,Se,Tl	100 & 10	100, 50, 25, 10, 2.5, 0.0
V	200 & 10	200, 100, 50, 10, 5.0, 0.0

3. Method detection limits (MDL):
   As = 0.25 ug/g (2.5 ug/L)   Tl = 0.25 ug/g (2.5 ug/L)
   Pb = 0.50 ug/g (5.0 ug/L)   V = 0.75 ug/g (7.5 ug/L)
   Se = 0.25 ug/g (2.5 ug/L)
4. Matrix modifier: 500 ppm $Pd(NO_3)_2$.
5. Analyze the standard curve. The cc must be > 0.995.
6. Analyze the ICV. If the ICV is not within $\pm$ 10% of the true value, the calibration standards should be prepared again and reanalyzed and/or the instrument conditions optimized again.
7. Analyze the reagent blank. If the reagent blank is greater than twice the MDL, redigest the samples or provide an adequate explanation as to why the samples should be acceptable.
8. Analyze the method blank, low-level spike, high-level spikes, samples and sample spikes.
9. Duplicate burns are required for each sample and standard with the average reported as the final result. Note: If the RPD between the two consecutive burns is greater than 20% for a sample whose concentration exceeds twice the detection limit, reanalyze the sample. If upon reanalysis the RPD between the two consecutive burns is still greater than 20%, the reported concentration for that sample should be qualified as having a possible interference.
10. If the concentration measured for any sample is greater than the highest standard, the sample must be diluted and reanalyzed.
11. A blank analysis (CCB) and calibration check (CCV) should be performed after every 10 samples and at the end of the run. If the blank is greater than twice the detection limit or the CCV is not within $\pm$ 10%, the standard curve must be reanalyzed and the analysis of any samples run since the last acceptable CCV and CCB must be repeated.
12. Interference tests:
    a. For each analytical batch select one typical sample whose concentration is at least 25 times the instrument detection limit. Dilute the sample (1+4). If the diluted sample does not agree within 10% of the original sample, MSA must be performed on all samples in the batch.
    b. If all samples in the batch are less than 25 times the instrument detection limit, select one sample for a post digestion (analytical) spike. Add 1 mL of the high standard to 1 mL of the sample. If the recovery is not within 15% of the true value, MSA must be performed on all samples.
    c. When MSA is required, three 5.0 mL aliquots of sample are spiked with 20, 40, and 60 uL respectively of a 5.0 mg/L MSA solution. Analyze each spike, and calculate the slope, x-intercept, y-intercept and correlation coefficient (CC) for each set. If the CC is less than 0.995, repeat the analysis once.

Number	TITLE	QC REFERENCE
USAEC No.s:	Soils & Sediments by GFAA (As, Pb, Se, Tl, & V)	USAEC/SW846

ESE DATA ENTRY

1. Upload data into CLASS (Chemical Laboratory Analysis and Scheduling System) data batch. CLASS is ESE's computerized data management system.
2. If the method blank has a response greater than the instrument detection limit, blank correction should be applied to the daily control spikes only. If the MB (or any sample with a matrix spike) has a negative response or is less than the instrument detection limit, enter the response as 0 Final.
3. Use 10X the actual standard soil weight for the method blank and control spike calculations.
4. Digestate volumes (0.1 L), weights (g) and % moisture should be supplied by CLASS. Verify the entries are correct. Responses should be uploaded in ug/L. (% Moisture for standard soil = 0.05). Include the sample %moisture summary in the data batch.
5. Post digestion spikes should have a dilution factor of 2 and a target equal to the high standard.
6. Generate spike recovery/control chart data for Information Services.

ATTACHMENT 2.0 -TYPICAL GFAA RUN SEQUENCE

Typical Furnace Run Sequence
USAEC/SW846 Samples

Blank	
Standard 1 (2.5 ug/L)	
Standard 2 (10.0 ug/L)	
Standard 3 (25.0 ug/L)	
Standard 4 (50.0 ug/L)	
Standard 5 (100 ug/L)	
Initial calibration verification - ICV (reference)	± 10%
Method blank (MB)	
Low spike (SP1)	see control charts
High spike (SP2)	see control charts
High spike (SP3)	see control charts
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike dup	
Sample #2	
CCV (50 ug/L)	± 10%
Continuing calibration blank - CCB	
Sample #3 through #12	
CCV (50 ug/L)	± 10%
CCB	
Sample #13 through #20	
Serial Dilution (1+4)	± 10%
or Post-Digestion Spike (SPX)	± 15%
CCV (50 ug/L)	± 10%
CCB	
MSA - 0	
MSA - 1	
MSA - 2	
MSA - 3	
CCV (50 ug/L)	± 10%
CCB	

ATTACHMENT 3.0 - MDL STUDY

October 27, 1993

GFAA Soil/Sediment MDL Study
January 1993

Element	Spike Conc. (ug/L)	Spike Conc. (ug/g)	ERA-Unspiked Response (ug/g)	ERA-Spike Response (ug/L)	ERA-Spike Weight (g)	ERA-Spike Response (ug/g)	Standard Deviation (ug/g)	ERA Soil MDL (ug/g)	AEC-Unspiked Response (ug/g)	AEC-Spike Response (ug/L)	AEC-Spike Weight (g)x10	AEC-Spike Response (ug/g)	Standard Deviation (ug/g)	AEC Soil MDL (ug/g)	Combined Reported MDL (ug/~~L~~g)
Vanadium 5100A	10.0	0.10	0.1662	12.9	1.0128	1.2737	0.0771	0.242	0.6508	31.8	1.165	2.7296	0.237	0.74	0.75
				13.0	1.0093	1.2880				30.0	1.017	2.9499			
				12.3	1.0064	1.2222				31.1	1.009	3.0823			
				11.6	1.0225	1.1345				26.6	1.064	2.5000			
				12.8	1.0194	1.2556				28.5	1.093	2.6075			
				10.9	1.0079	1.0815				29.7	1.014	2.9290			
				12.6	1.0124	1.2446				32.0	1.027	3.1159			
5100B	10.0	0.10	0.1760	11.5	1.0128	1.1355	0.0752	0.236	0.5775	37.5	1.165	3.2189	0.239	0.75	
				13.2	1.0093	1.3078				34.1	1.017	3.3530			
				12.4	1.0064	1.2321				34.4	1.009	3.4093			
				13.3	1.0225	1.3007				29.6	1.064	2.7820			
				13.0	1.0194	1.2753				32.8	1.093	3.0009			
				11.3	1.0079	1.1211				34.6	1.014	3.4122			
				12.4	1.0124	1.2248				31.4	1.027	3.0574			
5100C	10.0	0.10	0.0000	8.6	1.0128	0.8491	0.1212	0.381	0.3850	33.1	1.165	2.8412	0.234	0.74	
				9.4	1.0093	0.9313				30.1	1.017	2.9597			
				8.6	1.0064	0.8545				31.9	1.009	3.1615			
				6.9	1.0225	0.6748				25.6	1.064	2.4060			
				9.8	1.0194	0.9613				31.7	1.093	2.9003			
				7.9	1.0079	0.7838				30.3	1.014	2.9882			
				6.5	1.0124	0.6420				30.4	1.027	2.9601			
4100	10.0	0.10	0.0000	6.5	1.0128	0.6418	0.0307	0.097	0.4308	25.9	1.165	2.2232	0.083	0.26	
				6.6	1.0093	0.6539				23.0	1.017	2.2616			
				7.0	1.0064	0.6955				23.6	1.009	2.3389			
				6.7	1.0225	0.6553				22.2	1.064	2.0865			
				6.4	1.0194	0.6278				23.3	1.093	2.1317			
				6.2	1.0079	0.6151				22.3	1.014	2.1992			
				6.1	1.0124	0.6025				23.0	1.027	2.2395			

Reference: 40 CFR 136, Appendix B (ERA Inorganic Blank Sand & AEC Standard Soil)/SW846

GMDLSOIL

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

AMMONIA IN WATER BY TRAACS
(EPA METHOD 350.1)
USAEC METHOD - ANA1 - WATER

TABLE OF CONTENTS

**TITLE: AMMONIA IN WATER BY TRAACS (EPA METHOD 350.1)
USAEC METHOD - ANA1 - WATER**

1.0 SCOPE AND APPLICATION

1.1 Analytes

1.1.1 This ESE Standard Operating Procedure (SOP) follows EPA 350.1 protocols with additional quality control requirements applicable for the Class 1 analysis under United States Army Environmental Center (USAEC) guidelines for implementation of ER1110-1-263.

1.1.2 This SOP is applicable to the quantitative determination of ammonia in water samples.

1.2 Reporting Limits, Lower and Upper Standard Range and Chemical Abstract Service (CAS) Numbers

The reporting limits, lower and upper standard range and CAS number are:

Parameter	Reporting Limit (mg/L)	Lower Standard Range (mg/L)	Upper Standard Range (mg/L)	CAS Number
Ammonia (NH_3)	0.05	0.05	2.0	7664-41-7

1.3 Analysis Rate

After instrument calibration, one analyst can analyze approximately 90 water samples in an 8 hour day.

1.4 Safety Information

General laboratory safety applies. Proper laboratory apparel must be worn at all times. No special precautions are required unless the samples are hazardous.

1.5 Summary of Method

Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside and this color is measured colorimetrically.

1.6 Method Interferences

1.6.1 Turbidity and/or sample coloration that absorbs light near 660 nm will present a positive bias. Samples showing a high amount of suspended matter may be filtered through 0.45 um filters to help alleviate positive bias due to light scatter. When this is done, a note should be included in the lab notebook indicating that a filtration step was performed.

1.6.2 Ammonia is ubiquitous in the environment and may easily contaminate samples. It is a respiration product of the human body. Floor strippers and waxes commonly contain ammonia and are, therefore, a potential contamination source. Ammonia containing products should be prohibited in the laboratory area where ammonia analyses are performed. To help avoid contamination, wash sample cups with Type I water prior to use and rinse the cups again with a portion of the standard or sample to be analyzed. Avoid allowing sample cups, that contain any solutions, to sit for prolonged periods prior to analysis. By keeping a dust cover over the sample tray during analysis, the likelihood of ammonia contamination can be reduced.

1.6.3 High concentrations of calcium and magnesium ions can cause precipitation problems. A 5% EDTA solution helps suppress precipitation by chelating these metal cations.

2.0 APPARATUS AND MATERIALS

2.1 Technicon TRAACS 800 Autoanalyzer, consisting of the following:

2.1.1 Multitest cartridge.

2.1.2 10 mm by 0.5 mm ID flow cell.

2.1.3 660 nm filter.

2.1.4 37° C, 2.3 mL heater.

2.2 Glassware/Hardware:

2.2.1 Class A volumetric flasks - 50, 100, 250 and 1000 mL.

2.2.2 Class A volumetric pipets - 0.5, 1.0, 2.0 and 10.0 mL.

2.2.3 Analytical balance capable of weighing to 0.1 g.

2.3 Reagents

2.3.1 Sodium Hydroxide (NaOH) solution, 10N: Place a heavy-duty 2-liter beaker containing approximately 500 mL of Type I water into a cool water bath. Slowly add 400 g of NaOH, while stirring continuously with a glass rod. Allow solution to cool. Pour solution into a 1 liter flask and dilute to volume with Type I water.

2.3.2 Sodium Hydroxide (NaOH) solution, 0.1N: Dilute 10 mL of the 1.0 N NaOH (Section 2.4.1) into 100 mL of Type I water.

CAUTION: Always use safety goggles, rubber gloves, and a laboratory apron.

2.3.3 Sulfuric Acid (H_2SO_4) solution, 0.1N: Slowly add 3 mL of concentrated sulfuric acid to 1 liter of Type I water.

2.3.4 Sodium Phenolate: Add 60 mL of 10N NaOH solution (use caution when handling 10N NaOH solutions) and 39 mL of a commercially prepared liquified phenol solution (approximately 89% phenol) to approximately 250 mL of Type I water. Allow the solution to cool and then dilute to 500 mL with Type I water.

2.3.5 Disodium ethylenediamine-tetraacetate (EDTA): Add 2.5 mL of 10N NaOH and 41.0 g EDTA to approximately 800 mL of Type I water. Dissolve completely and dilute to 1 liter. Filter solution if particles are present. Add 3.0 mL of Brij-35.

2.3.6 Sodium Hypochlorite solution: Mix 164 mL of a bleach solution containing 5.25% NaOCl (such as CLOROX) with 36 mL with Type I water. Since CLOROX is a proprietary product, its formulation is subject to change. The analyst must be alert in detecting any product variation that would be significant to its use in this procedure. Purchasing a sodium hypochlorite solution from a laboratory reagent supply company is inadvisable due to the difficulty in obtaining recently prepared solutions.

2.3.7 Sodium Nitroprusside: Dissolve 0.55 g of sodium nitroprusside in 300 mL of Type I water and dilute to 500 mL.

2.3.8 Sampler wash: Add 1.0 mL of Brij-35 to a liter of Type I water.

2.3.9 Ammonia Stock Solution, 1000 mg/L NH_3-N: Dissolve 3.819 g of anhydrous ammonium chloride (NH_4Cl), dried at 105°C, in Type I water and dilute to 1 liter.

2.3.10 Ammonia Control Stock, 100 mg/L NH_3-N: Dissolve 0.3819 g of anhydrous ammonium chloride (NH_4Cl), dried at 105°C, in Type I water and dilute to 1 liter.

NOTE: It is recommended that this solid NH_4Cl reagent be obtained from a different source supplier than the NH_4Cl used for making the Ammonia Stock Solution (Section 2.3.9). However, if the solid NH_4Cl reagent to be used is obtained from the same manufacturer, it must be from a different lot than the Ammonia Stock Solution.

2.3.11 Intermediate Ammonia Standard, 10 mg/L NH_3-N: Add 1.00 mL Ammonia Stock Solution (Section 2.3.9) to a 100 mL volumetric flask and dilute to volume with Type I water.

2.3.12 Ammonia Control solution, 10.0 mg/L NH_3-N: Add 10.0 mL Ammonia Control Stock (Section 2.3.10) to a 100 mL volumetric flask and dilute to volume with Type I water.

2.3.13 Prepare working calibration standards by pipeting the following volumes of the stock or intermediate ammonia standard with an eppendorf pipet. End volume for all standards is 100 mL.

Volume of Stock or Intermediate Ammonia Standard (mL)	Concentration of Ammonia Standard (mg/L)
0.0	0.0
0.5 (Intermediate)	0.05
1.0 (Intermediate)	0.10
2.5 (Intermediate)	0.25
5.0 (Intermediate)	0.50
0.1 (Stock)	1.00
0.2 (Stock)	2.00

2.3.14 Ammonia Control solution, 1.00 mg/L NH_3-N: Add 1.0 mL Ammonia Control Stock (Section 2.3.10) to a 100 mL volumetric flask and dilute to volume with Type I water.

3.0 SAMPLE HANDLING AND STORAGE

3.1 Sampling Procedure - Samples are preserved with concentrated sulfuric acid (H_2SO_4) to a pH $\leq$ 2.

3.2 Containers - Sampling containers used for this method are 1 L plastic cubitainers.

3.3 Storage Conditions - Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4°C.

3.4 Holding Time Limit - The holding time for water samples, that are preserved, is 28 days from the time of sampling to the time of analysis.

4.0 CALIBRATION

4.1 Initial Calibration

The instrument is standardized by analyzing the calibration standards specified in Section 2.3.13 and a blank. The absorbance is read at 660 nm and the peak area are compared to the standard peak area. The linear regression equation is determined for concentration versus response.

4.2 Calibration Checks

4.2.1 Calibration Check Standard/Initial Calibration Verification (ICV) - An ICV (a known reference standard) must be analyzed after the calibration standards. The ICV is prepared from a commercially available certified reference standard. The concentration of the ICV will vary from lot to lot but should be near the upper range of the standard curve. The acceptance criteria of the ICV is ± 15 % of the known concentration.

4.2.2 Continuing Calibration Verification Standard - A Continuing Calibration Verification Standard (CCV) must be analyzed after every ten (10) samples and at the end of analysis. The CCV is the 1.00 mg/L standard. The recovery based on the standard curve must be within 15 % of the known value.

4.2.3 If the recovery of the reference standard or CCV does not meet the acceptance criteria, the standard must be rerun. If either standard still fails, the samples analyzed since the last acceptable reference standard

or CCV must be rerun. If the samples are reanalyzed and the CCV still fails, then your Department Manager and the Laboratory Coordinator must be notified. The Laboratory Coordinator will notify USACE to determine further action.

4.3 Daily Calibration

For daily calibration, an initial calibration curve and QC checks will be performed as indicated in Sections 4.1 and 4.2.

5.0 PROCEDURE

Daily control spike samples (Section 7.3) and environmental samples are prepared and analyzed as follows:

5.1 Separations - There is no separation stage in this method.

5.2 Chemical Reaction - Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional the ammonia concentration. The blue color is intensified with sodium nitroprusside.

5.3 Instrument Analysis

5.3.1 Check sample pH and neutralize any samples with pH that is not between 5 - 9 with 0.1 N NaOH or 0.1 N H_2SO_4.

5.3.2 Turn on the valve supplying air to the TRAACS. Adjust the regulator inside the TRAACS to read 22 psi.

5.3.3 Be sure to check that there are enough reagents for an analytical run.

5.3.4. With fresh DI water, place the platen on the pump and start pumping DI water through the TRAACS.

5.3.5. After approximately 10 minutes of pumping DI water, when it is apparent that a good bubble pattern is present, turn on the autoclave to allow reagents to start pumping through the TRAACS.

5.3.6 After the reagents have been pumping through the TRAACS for at least 20 minutes, check the baseline and full scale by analyzing a fresh cup of the high standard (2.00 mg/L).

5.3.7 Compare the values obtained of baseline and full scale to previous baseline and full scale values. A high baseline and full scale value can indicate contaminated reagents.

5.3.8. Place standards in the sampler in order of increasing concentration to eliminate carryover.

5.3.9 Analyze the daily quality control samples and reference sample.

5.3.10 Analyze the samples. Be sure to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) after every 10 samples.

5.3.11 Dilute samples that have concentrations exceeding the upper standard range and reanalyze.

5.3.12 End the run with a CCV and CCB to ensure that instruments have maintained stability throughout the run.

6.0 CALCULATION

6.1 The peak area of each of the calibration standards is measured by the TRAACS software and uploaded into CLASS™ (Chemical Laboratory Analysis and Scheduling System - ESE's software system for managing laboratory data). CLASS™ uses the standard responses to develop the best quadratic regression fit by relating the concentration of the standards to the peak area. The correlation coefficient of the curve must be ≥ 0.995.

6.2 The sample and quality control standard response and dilution factor, if any, are uploaded into CLASS™ from the TRAACS. The quadratic regression equation, in Section 6.1, is applied to the peak area obtained for the samples and quality control standards to determine the concentration of ammonia in mg/L.

7.0 DAILY QUALITY CONTROL

7.1 Method blanks (MB) must be analyzed with every lot. The Method Blank is Type I water. Follow the same procedure used for the samples.

7.2 A Continuing Calibration Blank (CCB) must be analyzed after every 10 samples. The CCB is Type I water.

7.3 The following daily control spike samples are prepared by adding the following volumes of the control stock (Section 2.3.8) or intermediate control solution (Section 2.3.10) to 100 mL of Type I water.

Daily Control Spike Sample Prepared	Volume (mL) of AEC Stock or Intermediate Spike Solution Spiked into 100 mL	Concentration of Control Spike Solution (mg/L)
Blank	0	0
Low	1.0 (Intermediate)	0.1
High	0.1 (Stock)	1.0
High	0.1 (Stock)	1.0

7.4 The Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) are not required for AEC projects, but will be analyzed if required by the contract or project. The SPM and SPMD (0.5 mg/L) are made by pipeting 1 mL of the 1.00 mg/L Ammonia Control (Section 2.3.12) solution into 1.0 mL of sample.

7.5 Control Charts

7.5.1 Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control. Control charts are prepared for each target analyte using percent recovery data from the spiked QC samples (low and high level).

$$\% \text{ Recovery} = \frac{\text{Found Concentration - Method Blank}}{\text{Spiked Concentration}} \times 100$$

7.5.2 To prepare control charts, the analyst will submit a data batch including spike and method blank samples to Information Services after analysis. Information Services will put the information into the USAEC control chart program. The following control charts will be returned to the analysts.

7.5.2.1 Average (x) percent recovery for the two high concentration spiked QC samples in each lot,

7.5.2.2 Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,

7.5.2.3 Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and

7.5.2.4 Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

7.5.3 The average (x), average range (R) and control limits for x and R shall be updated after each lot for the first 20 in control lots. Limits established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 in control lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

8.0 REFERENCE

Methods for Chemical Analysis of Water and Wastes (EPA Method 350.1), EPA-600/4-79-020, Revised March 1983.

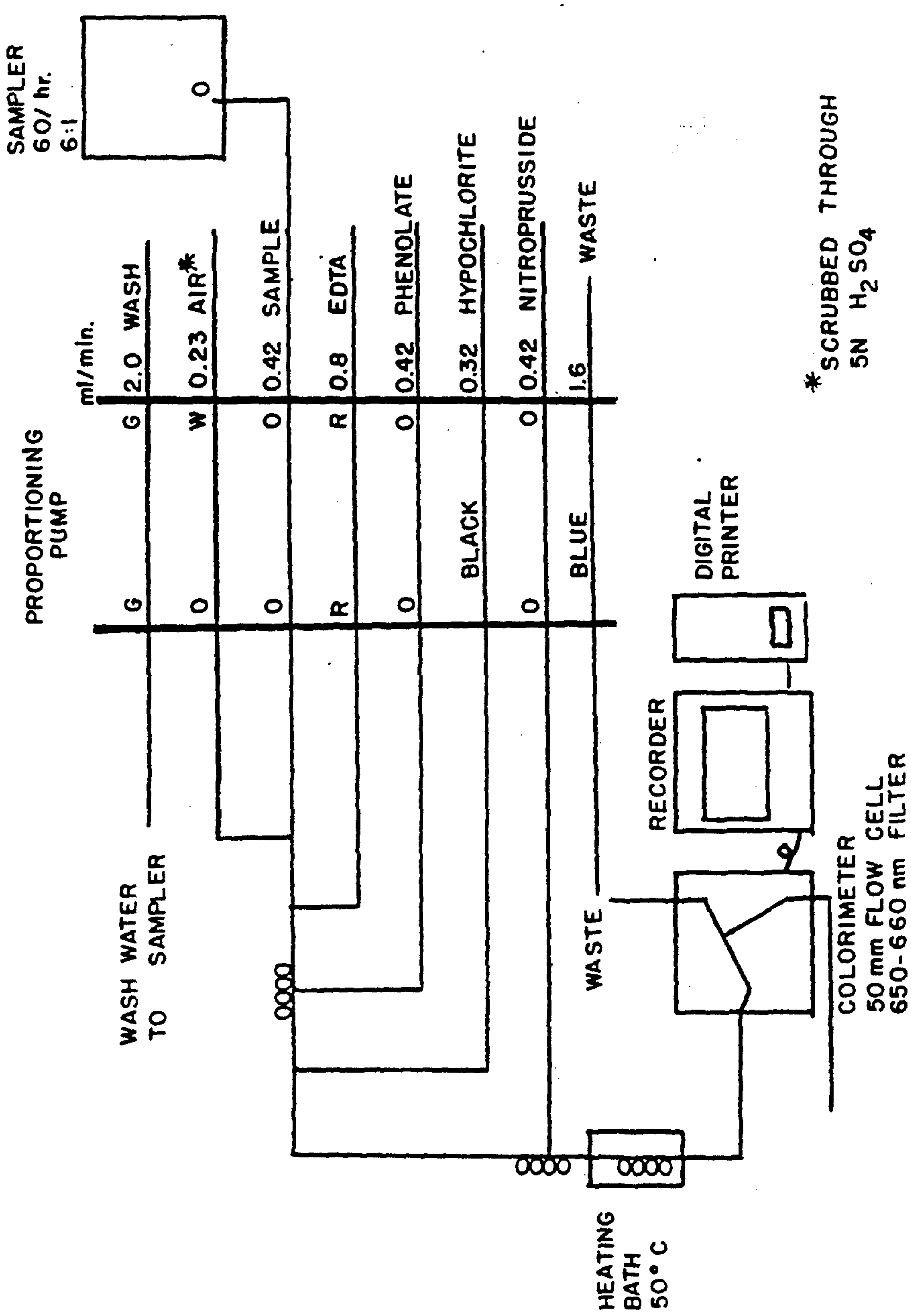
9.0 ATTACHMENTS

9.1 Attachment A - **AMMONIA MANIFOLD**

9.2 Attachment B - **TYPICAL TECHNICON TRAACS RUN SEQUENCE**

9.3 Attachment C - **METHOD DETECTION LIMIT STUDY**

Attachment A - AMMONIA MANIFOLD



Attachment B - **TYPICAL TECHNICON TRAACS RUN SEQUENCE**

Calibration Standard (2.0 mg/L)	
Blank	
Standard 1 (MDL)	
Standard 2	
Standard 3	
Standard 4	
Standard 5	
Standard 6	
Initial calibration blank - ICB	
Initial calibration verification - ICV (reference)	± 15%
Method blank (prep blank)	
Low Spike - SP1	
High Spike - SP2	
High Spike - SP3	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike duplicate	
Sample #2	
Sample #3	
Sample #4	
Continuing calibration blank - CCB	
Continuing calibration verification - CCV	± 15%
Sample #5	
.	
.	
.	
Sample #14	
CCB	
CCV	± 15%
Sample #15	
.	
.	
.	
Sample #24	
CCB	
CCV	± 15%
.	
.	

Attachment C - **METHOD DETECTION LIMIT STUDY**

December 23, 1993

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

AMMONIA IN SOIL BY TRAACS (MODIFIED EPA METHOD 350.1) USAEC METHOD - ANA1 - SOIL

TABLE OF CONTENTS

TITLE: **AMMONIA IN SOIL BY TRAACS (MODIFIED EPA METHOD 350.1) USAEC METHOD - ANA1 - SOIL**

1.0 SCOPE AND APPLICATION

1.1 Analytes

1.1.1 This ESE Standard Operating Procedure (SOP) follows EPA 350.1 protocols with additional quality control requirements applicable for the Class 1 analysis under United States Army Environmental Center (USAEC) guidelines for implementation of ER1110-1-263.

1.1.2 This SOP is applicable to the quantitative determination of ammonia in soil samples.

1.2 Reporting Limits, Lower and Upper Standard Range and Chemical Abstract Service (CAS) Numbers

The reporting limits, lower and upper standard range and CAS number are:

Parameter	Reporting Limit (ug/g)	Lower Standard Range (mg/L)	Upper Standard Range (mg/L)	CAS Number
Ammonia (NH3)	6.25	0.05	2.0	7664-41-7

1.3 Analysis Rate

One analyst can distill approximately 36 soil samples in an 8 hour day.

1.4 Safety Information

General laboratory safety applies. Proper laboratory apparel must be worn at all times. No special precautions are required unless the samples are hazardous.

1.5 Summary of Method

Total ammonia of solid matrices can be determined by placing 2.0 g of a soil sample, 200 mL of Type I water and 50 mL of 1 N NaOH in a distillation flask. Then, the sample is distilled into 50 mL of 2% boric acid for approximately 20-30 minutes, until approximately 200 mL of distillate is collected. Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside and this color is measured colorimetrically.

1.6 Method Interferences

1.6.1 Turbidity and/or sample coloration that absorbs light near 660 nm will present a positive bias. Samples showing a high amount of suspended matter may be filtered through 0.45 um filters to help alleviate positive bias due to light scatter. When this is done, a note should be included in the lab notebook indicating that a filtration step was performed.

1.6.2 Ammonia is ubiquitous in the environment and may easily contaminate samples. It is a respiration product of the human body. Floor strippers and waxes commonly contain ammonia and are, therefore, a potential contamination source. Ammonia containing products should be prohibited in the laboratory area where ammonia analyses are performed. To help avoid contamination, wash sample cups with Type I water prior to use and rinse the cups again with a portion of the standard or sample to be analyzed. Avoid allowing sample cups, that contain any solutions, to sit for prolonged periods prior to analysis. By keeping a dust cover over the sample tray during analysis, the likelihood of ammonia contamination can be reduced.

1.6.3 High concentrations of calcium and magnesium ions can cause precipitation problems. A 5% EDTA solution helps suppress precipitation by chelating these metal cations.

2.0 APPARATUS AND MATERIALS

2.1 Distillation apparatus: An 800 mL Kjeldahl flask attached to a vertical condenser so that the outlet tip is submerged below the surface of the receiving acid solution. The distillation apparatus is sold in parts in laboratory supply catalogs.

2.2 Technicon TRAACS 800 Autoanalyzer, consisting of the following:

2.2.1 Multitest cartridge.

2.2.2 10 mm by 0.5 mm ID flow cell.

2.2.3 660 nm filter.

2.2.4 37° C, 2.3 mL heater.

2.3 Glassware/Hardware:

2.3.1 Class A volumetric flasks - 50, 100, 250 and 1000 mL.

2.3.2 Class A volumetric pipets - 0.5, 1.0, 2.0 and 10.0 mL.

2.3.3 Analytical balance capable of weighing to 0.1 g.

2.4 Reagents

2.4.1 Sodium Hydroxide (NaOH) solution, 1N: Slowly add 40 g of NaOH, while stirring, into 500 mL of Type I water. Allow solution to cool. Pour solution into a 1 liter flask and dilute to volume with Type I water.

2.4.2 Sodium Hydroxide (NaOH) solution, 0.1N: Dilute 10 mL of the 1.0 N NaOH (Section 2.4.1) into 100 mL of Type I water.

CAUTION: Always use safety goggles, rubber gloves, and a laboratory apron.

2.4.3 Sulfuric Acid (H_2SO_4) solution, 0.1N: Slowly add 3 mL of concentrated sulfuric acid to 1 liter of Type I water.

2.4.4 Boric Acid solution, 2%: Dissolve 20 g of boric acid into 800 mL of Type I water and dilute to 1 L.

2.4.5 Sodium Phenolate: Add 60 mL of 10N NaOH solution (use caution when handling 10N NaOH solutions) and 39 mL of a commercially prepared liquified phenol solution (89 % phenol) to approximately 250 mL of Type I water. Allow the solution to cool and then dilute to 500 mL with Type I water.

2.4.6 Disodium ethylenediamine-tetraacetate (EDTA): Add 2.5 mL of 10N NaOH and 41.0 g EDTA to approximately 800 mL of Type I water. Dissolve completely and dilute to 1 liter. Filter solution if particles are present. Add 3.0 mL of Brij-35.

2.4.7 Sodium Hypochlorite solution: Mix 164 mL of a bleach solution containing 5.25% NaOCl (such as CLOROX) with 36 mL with Type I water. Since CLOROX is a proprietary product, its formulation is subject to change. The analyst must be alert in detecting any product variation that would be significant to its use in this procedure. Purchasing a sodium hypochlorite solution from a laboratory reagent supply company is inadvisable due to the difficulty in obtaining recently prepared solutions.

2.4.8 Sodium Nitroprusside: Dissolve 0.55 g of sodium nitroprusside in 300 mL of Type I water and dilute to 500 mL.

2.4.9 Sampler wash: Add 1.0 mL of Brij-35 to a liter of Type I water.

2.4.10 Ammonia Stock Solution, 1000 mg/L NH_3-N: Dissolve 3.819 g of anhydrous ammonium chloride (NH_4Cl), dried at 105°C, in Type I water and dilute to 1 liter.

2.4.11 Ammonia Control Stock, 1000 mg/L NH_3-N: Dissolve 3.819 g of anhydrous ammonium chloride (NH_4Cl), dried at 105°C, in Type I water and dilute to 1 liter.

NOTE: It is recommended that this solid NH_4Cl reagent be obtained from a different source supplier than the NH_4Cl used for making the Ammonia Stock Solution (Section 2.4.10). However, if the solid NH_4Cl reagent to be used is obtained from the same manufacturer, it must be from a different lot than the Ammonia Stock Solution.

2.4.12 Intermediate Ammonia Standard, 10 mg/L NH_3-N: Add 1.00 mL Ammonia Stock Solution (Section 2.4.10) to a 100 mL volumetric flask and dilute to volume with Type I water.

2.4.13 Intermediate Ammonia Control solution, 100 mg/L NH_3-N: Add 10.0 mL Ammonia Control Stock (Section 2.4.11) to a 100 mL volumetric flask and dilute to volume with Type I water.

2.4.14 Prepare working calibration standards by pipeting the following volumes of the stock or intermediate ammonia standard with an eppendorf pipet. End volume for all standards is 100 mL.

Volume of Stock or Intermediate Ammonia Standard (mL)	Concentration of Ammonia Standard (mg/L)
0.0	0.0
0.5 (Intermediate)	0.05
1.0 (Intermediate)	0.10
2.5 (Intermediate)	0.25
5.0 (Intermediate)	0.50
0.1 (Stock)	1.00
0.2 (Stock)	2.00

3.0 SAMPLE HANDLING AND STORAGE

3.1 Sampling Procedure - Samples for ammonia analysis shall be placed in cleaned, wide-mouthed, glass jar with a Teflon lined lid. Sample jars shall be placed in a temperature-controlled [4°C] chest immediately following sampling and delivered to the laboratory as soon as possible.

3.2 Containers - Sampling containers used for this method are 1 L wide-mouthed, glass bottle.

3.3 Storage Conditions - Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4°C.

3.4 Holding Time Limit - The holding time for soil samples is 28 days from the time of sampling to the time of analysis.

4.0 CALIBRATION

4.1 Initial Calibration

The instrument is standardized by analyzing the calibration standards specified in Section 2.4.14 and a blank. The absorbance is read at 660 nm and the peak area are compared to the standard peak area. The linear regression equation is determined for concentration versus response.

4.2 Calibration Checks

4.2.1 Calibration Check Standard/Initial Calibration Verification (ICV) - An ICV (a known reference standard) must be analyzed after the calibration standards. The ICV is prepared from a commercially available certified reference standard. The concentration of the ICV will vary from lot to lot but should be near the upper range of the standard curve. The acceptance criteria of the ICV is ± 15 % of the known concentration.

4.2.2 Continuing Calibration Verification Standard - A Continuing Calibration Verification Standard (CCV) must be analyzed after every ten (10) samples and at the end of analysis. The CCV is the 1.0 mg/L standard. The recovery based on the standard curve must be within 15 % of the known value.

4.2.3 If the recovery of the reference standard or CCV does not meet the acceptance criteria, the CCV or reference standard must be rerun. If reanalysis of the CCV or reference standard is outside of criteria, the samples analyzed since the last acceptable reference standard or CCV must be rerun. If the samples are reanalyzed and the CCV still fails, then your Department Manager and the Laboratory Coordinator must be notified. The Laboratory Coordinator will notify USACE to determine further action.

4.3 Daily Calibration

For daily calibration, an initial calibration curve and QC checks will be performed as indicated in Sections 4.1 and 4.2.

5.0 PROCEDURE

Daily control spike samples (Section 7.3) and environmental samples are prepared and analyzed as follows:

5.1 Distillation

5.1.1 Pre-steam the distillation apparatus by distilling 100 mL of Type I water prior to distilling samples.

5.1.2 Place 2.0 g of the soil sample into an 800 mL Kjeldahl flask. Add several boiling chips and 200 mL of Type I water to the Kjeldahl flask.

5.1.3 Add 50 mL of the 2 % boric acid (Section 2.4.4) to a pre-weighed receiving flask.

5.1.4 Connect the receiving flask and condenser and then add 50 mL of the 1 N NaOH to the Kjeldahl flask (Note: Be sure to add the NaOH after the receiving flask is connected to minimize the volatilization of ammonia).

5.1.5 Distill at the rate of 5-10 mL/min into the 50 mL of 2 % boric acid. Collect approximately 200 mL of distillate.

5.1.6 Reweigh the receiving flask to determine final volume by weight.

5.2 Chemical Reaction - Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional the ammonia concentration. The blue color is intensified with sodium nitroprusside.

5.3 Instrument Analysis

5.3.1 Check distillate pH and neutralize any samples with pH that is not between 5 - 9 with 0.1 N NaOH or 0.1 N H_2SO_4.

5.3.2 Turn on the valve supplying air to the TRAACS. Adjust the regulator inside the TRAACS to read 22 psi.

5.3.3 Be sure to check that there are enough reagents for an analytical run.

5.3.4. With fresh DI water, place the platen on the pump and start pumping DI water through the TRAACS.

5.3.5. After approximately 10 minutes of pumping DI water, when it is apparent that a good bubble pattern is present, turn on the autoclave to allow reagents to start pumping through the TRAACS.

5.3.6 After the reagents have been pumping through the TRAACS for at least 20 minutes, check the baseline and full scale by analyzing a fresh cup of the high standard (2.00 mg/L).

5.3.7 Compare the values obtained of baseline and full scale to previous baseline and full scale values. A high baseline and full scale value can indicate contaminated reagents.

5.3.8. Place standards in the sampler in order of increasing concentration to eliminate carryover.

5.3.9 Analyze the daily quality control samples and reference sample.

5.3.10 Analyze the samples. Be sure to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) after every 10 samples.

5.3.11 Dilute samples that have concentrations exceeding the upper standard range and reanalyze.

5.3.12 End the run with a CCV and CCB to ensure that instruments have maintained stability throughout the run.

6.0 CALCULATION

6.1 The peak area of each of the calibration standards is measured by the TRAACS software and uploaded into CLASS™ (Chemical Laboratory Analysis and Scheduling System - ESE's software system for managing laboratory data). CLASS™ uses the standard responses to develop the best quadratic regression fit by relating the concentration of the standards to the peak area. The correlation coefficient of the curve must be ≥ 0.995.

6.2 The sample and quality control standard response and dilution factor, if any, are uploaded into CLASS™ from the TRAACS. The quadratic regression equation, in Section 6.1, is applied to the peak area obtained for the samples and quality control standards to determine the concentration of ammonia in the distillated sample.

6.3 Sample weight (in grams), distillate end volume and percent moisture are entered into CLASS™ manually and are used to calculate the final sample concentration in ug/g.

7.0 DAILY QUALITY CONTROL

7.1 Method blanks (MB) must be analyzed with every lot. The Method Blank is 2 g of AEC soil. Follow the same procedure used for the samples.

7.2 A Continuing Calibration Blank (CCB) must be analyzed after every 10 samples. The CCB is Type I water.

7.3 The following daily control spike samples are prepared by adding the following volumes of the intermediate control solution (Section 2.4.13) to 2.0 g of AEC standard soil.

Daily Control Spike Sample Prepared	Volume (mL) of AEC Intermediate Spike Solution Spiked into 2 g	Concentration of Control Spike Solution (ug/g)
Blank	0	0
Low	0.25	12.5
High	2.5	125
High	2.5	125

7.4 The Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) are not required for AEC projects, but will be analyzed if required by the contract or project. The SPM and SPMD are made by pipeting 2.5 mL of the 100 mg/L Ammonia Control (Section 2.4.13) solution onto 2 g of sample.

7.5 Control Charts

7.5.1 Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control. Control charts are prepared for each target analyte using percent recovery data from the spiked QC samples (low and high level).

$$\% \text{ Recovery} = \frac{\text{Found Concentration - Method Blank}}{\text{Spiked Concentration}} \times 100$$

7.5.2 To prepare control charts, the analyst will submit a data batch including spike and method blank samples to Information Services after analysis. Information Services will put the information into the USAEC control chart program. The following control charts will be returned to the analysts.

7.5.2.1 Average (x) percent recovery for the two high concentration spiked QC samples in each lot,

7.5.2.2 Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,

7.5.2.4 Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and

7.5.2.4 Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

7.5.3 The average (x), average range (R) and control limits for x and R shall be updated after each lot for the first 20 in control lots. Limits established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 in control lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

8.0 REFERENCE

Methods for Chemical Analysis of Water and Wastes (EPA Method 350.1), EPA-600/4-79-020, Revised March 1983.

9.0 ATTACHMENTS

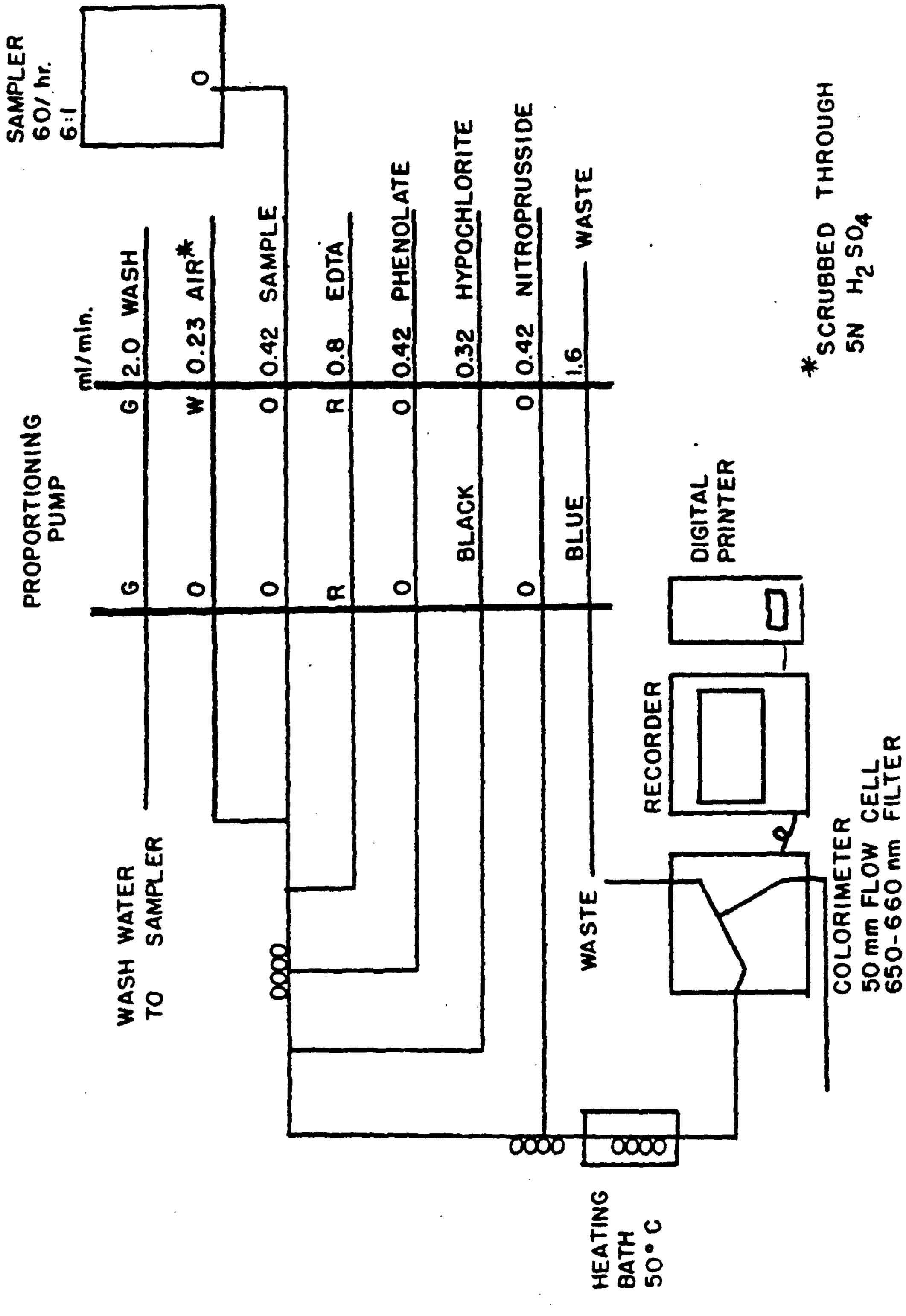
9.1 Attachment A - **AMMONIA MANIFOLD**

9.2 Attachment B - **TYPICAL TECHNICON TRAACS RUN SEQUENCE**

9.3 Attachment C - **DEVIATION FROM METHOD 350.1**

9.4 Attachment D - **METHOD DETECTION STUDY**

Attachment A - AMMONIA MANIFOLD



October 27, 1993

Attachment B - **TYPICAL TECHNICON TRAACS RUN SEQUENCE**

Calibration Standard (2.0 mg/L)	
Blank	
Standard 1 (MDL)	
Standard 2	
Standard 3	
Standard 4	
Standard 5	
Standard 6	
Initial calibration blank - ICB	
Initial calibration verification - ICV (reference)	± 15%
Method blank (prep blank)	
Low Spike - SP1	
High Spike - SP2	
High Spike - SP3	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike duplicate	
Sample #2	
Sample #3	
Sample #4	
Continuing calibration blank - CCB	
Continuing calibration verification - CCV	± 15%
Sample #5	
.	
.	
.	
Sample #14	
CCB	
CCV	± 15%
Sample #15	
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.	
Sample #24	
CCB	
CCV	± 15%
.	
.	

Attachment C - DEVIATION FROM METHOD 350.1

1. Soil and sediment matrices are not included in the scope of EPA Method 350.1. Therefore, EPA Method 350.1 has been modified for inclusion of soil and sediment samples in the method. The modifications made are only on the distillation procedure which are as follows:

   Two grams of a soil sample is used.

   A 200 mL volume of Type I water is added to the soil sample, along with 50 mL of 1 N NaOH.

   Fifty mL of 2 % boric acid is added to the receiving flask and the sample is distilled until 200 mL of the distillate is collected.

   The analysis procedure defined in the EPA method is then followed as written with no further deviations.

Attachment D - METHOD DETECTION STUDY

METHOD DETECTION LIMIT STUDY

Laboratory Name: Environmental Science & Engineering, Inc. (ESE)
Address: P.O. Box 1703, Gainesville, Florida, 32602-1703
Manager: Dr. John J. Mousa, Director, Gainesville Laboratory
Phone: (904) 332-3318

Method: Ammonia in soil - Modified EPA Method 350.1

Compound	R1 (mg/kg)	R2 (mg/kg)	R3 (mg/kg)	R4 (mg/kg)	R5 (mg/kg)	R6 (mg/kg)	R7 (mg/kg)	X (mg/kg)	S	MDL (mg/kg)
Ammonia	31.6	30.0	31.4	33.3	31.4	31.5	31.4	31.5	0.9	3.0

Note: Target concentration for ammonia in soil is approximately 31.25 mg/kg.
Actual target concentrations vary due to varying extract volumes and soil weight.

R = Actual concentration for each replicate 1-7
X = Average concentration
S = Standard deviation
mg/kg = milligram per kilogram

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

DETERMINATION OF NITRATE + NITRITE IN WATER BY TECHNICON (EPA METHOD 353.2) USAEC METHOD - ANA2 -WATER

TABLE OF CONTENTS

TITLE: **DETERMINATION OF NITRATE + NITRITE IN WATER BY TECHNICON (EPA METHOD 353.2)**
USAEC METHOD - ANA2 - WATER

1.0 SCOPE AND APPLICATION

1.1 Analytes

1.1.1 This ESE Standard Operating Procedure (SOP) follows EPA 353.2 protocols with additional quality control requirements applicable for the Class 1 analysis under United States Army Environmental Center (USAEC) guidelines for implementation of ER1110-1-263.

1.1.2 This SOP is applicable to the quantitative determination of nitrate + nitrite in water samples.

1.2 Reporting Limits, Lower and Upper Standard Range and Chemical Abstract Service (CAS) Numbers

The reporting limits, lower and upper standard range and CAS number are:

Parameter	Reporting Limit (mg/L)	Lower Standard Range (mg/L)	Upper Standard Range (mg/L)	CAS Number
Nitrate + Nitrite	0.02	0.02	1.0	*

* There is no CAS Number for Nitrate + Nitrite.

1.3 Analysis Rate

After instrument calibration, one analyst can analyze approximately 40 water samples in an 8-hour day.

1.4 Safety Information

General laboratory safety applies. Proper laboratory apparel must be worn at all times.

1.5 Summary of Method

By use of an autosampler and a proportioning pump, a sample is passed through a copper-coated cadmium column to reduce nitrate to nitrite. The sum of the reduced nitrite plus the nitrite originally present in the solution is determined by diazotizing with sulfanilamide and coupling with ethylenediamine dihydrochloride to produce an azo dye. The concentration of this azo dye is measured colorimetrically. The concentration of the azo dye is proportional to the original concentration of nitrogen in the sample that was in the form of nitrate and/or nitrite. Nitrite can be determined by eliminating the cadmium reduction column from the sampling train.

1.6 Method Interferences

1.6.1 Suspended matter in the samples can accumulate in the cadmium column and restrict flow. Since nitrate and nitrite are highly soluble in water, samples may be pre-filtered to remove suspended particulates.

1.6.2 High concentrations of iron, copper or other metals may produce low results. EDTA added to the samples can help to reduce this interference.

1.6.3 Sulfides adversely affect the performance of the cadmium column, producing low results.

1.6.4 The presence of oil or grease in a sample can produce low results by coating the surface of the cadmium granules and interfering with nitrite reduction.

2.0 APPARATUS AND MATERIALS

2.1 Technicon AutoAnalyzer II, consisting of the following:

2.1.1 Sampler IV: with 30/hour, 2/1 sample/wash ratio cam.

2.1.2 Proportioning Pump.

2.1.3 Nitrate Analytical Cartridge.

2.1.4 Colorimeter equipped with a 15 millimeter flowcell and 520 nanometer filters.

2.1.5 Strip-chart recorder.

2.2 Filtering apparatus.

2.3 AutoAnalyzer sample cups (disposable).

2.4 Assorted Class A volumetric flasks and pipettes.

2.5 Various automatic pipettes.

2.6 Reagents

2.6.1 Ammonium Chloride-EDTA Reagent: Dissolve 85 g of reagent NH_4Cl and 0.10 g disodium ethylenediamine tetraacetate in approximately 800 mL of Type I water. Adjust pH to 8.5 by adding approximately 7.0 mL 10 N NaOH and dilute to 1 liter. Add 0.5 mL Brij-35. Prepare fresh every 2 months.

2.6.2 Color Reagent: Add 40.0 g sulfanilamide, 2.0 g N-1-napthylethylenediamine dihydrochloride, and 100 mL concentrated phosphoric acid to approximately 800 mL Type I water. Dissolve completely and dilute to 1 liter. Store in a dark bottle. This solution is stable for 2 months.

2.6.3 Wash solution: Add 0.5 mL Brij-35 to 1 liter Type I water.

2.6.4 Conditioning Reagent (for cadmium column): Dissolve 22.0 g ammonium chloride, 15.0 g cupric sulfate ($CuSO_4 \cdot 5H_2O$) and 1.0 g EDTA in Type I water. Add 2.0 mL of 1000 mg/L Nitrate Stock Solution and dilute to 1 liter. Prepare fresh every 6 months.

2.6.5 Hydrochloric Acid (HCL) 1+1: Add 50 mL of concentrated HCL to a 100 mL volumetric flask and dilute to volume with Type I water.

2.6.6 Concentrate Eluent solution, 0.6 mM sodium bicarbonate/1.76 mM sodium carbonate: Dissolve 12.6 g of sodium bicarbonate and 46.64 g of sodium carbonate in reagent water and dilute to 2 liters.

2.6.7 Working Eluent solution: Dilute 16 mL of the Stock Eluent (Section 2.6.6) to 2 liters with reagent water.

2.6.8 Granulated cadmium, 40-60 mesh - Purchased from Alpkem Corporation. The cadmium granules (new or used) are cleaned with 1+1 HCl and copperized in the following fashion:

Place cadmium granules in a small beaker and add approximately 25 mL of 1+1 HCl. Swirl granules in a sonication bath until they appear silver.Decant the HCl solution and rinse thoroughly with approximately 500 mL of Type I water. Decant the Type I water and add 50 mL of conditioning reagent (Section 2.6.4). Swirl gently for 2 minutes, being careful not to expose the cadmium granules to air. Decant and repeat with another portion of conditioning reagent. Continue in this fashion until a brown colloidal precipitate just begins to form. The cadmium granules should appear black. Immediately decant all but about 10 mL of the solution and add approximately 50 mL of Type I water.

2.7 Preparation of reduction column

2.7.1 Place a glass wool plug in one end of a purple/black (P/N 116-0549P16) pump tube. Fill the tube with solution from the beaker which contains the prepared cadmium. Clamp off the end of the tube containing the glass wool plug.

2.7.2 Cut the end off of a blue Eppendorf pipet tip equal to the inside diameter of the tube and push it into the end of the pump tube opposite the glass wool plug.

2.7.3 Using a small scoop, start to fill the column, adding a few granules at a time. Roll the column between the fingers to aid in filling the column and to dislodge granules caught in the tube. Fill to within 1/4 of an inch of the top of the tube.

2.7.4 The cadmium column is now complete and may be stored until needed by fastening both ends of the column together with a plastic nipple. Avoid allowing any air to enter the column.

2.8 Stock and Calibration Standards

2.8.1 Stock Nitrate Solution, 1000 mg/L: Dissolve 7.2182 g anhydrous potassium nitrate, oven dried at 110° C for 1 hour, in approximately 500 mL of Type I water and dilute to 1 liter. Store at 4° C. This solution is stable for 6 months.

2.8.2 Nitrate Control Stock, 1000 mg/L: Dissolve 6.0681 g anhydrous sodium nitrate, oven dried at 110°C for 1 hour, in approximately 500 mL of Type I water and dilute to 1 liter. Store at 4° C. This solution is stable for 6 months.

2.8.3 Stock Nitrite Solution, 1000 mg/L: Dissolve 6.072 g anhydrous potassium nitrite (stored in a desiccator) in approximately 500 mL of distilled water and dilute to volume. Store at 4° C. This solution is not stable, prepare fresh daily.

2.8.4 Intermediate Nitrate Standard, 10 mg/L: Add 1.0 mL of Stock Nitrate Solution (Section 2.8.1) to a 100 mL volumetric flask and dilute to volume with distilled water. Prepare fresh weekly.

2.8.5 Intermediate Nitrate Control, 10 mg/L: Add 1.0 mL of Nitrate Control Stock (Section 2.8.2) to a 100 mL volumetric flask and dilute to volume with Type I water. Prepare fresh each week.

2.8.6 Working Standards: The following dilution scheme can be used to prepare the calibration standards by adding the Intermediate Nitrate Standard (Section 2.8.4) to 100 mL of Type I water. Prepare fresh each week.

Volume of Intermediate Nitrate Standard (mL)	Concentration of Nitrate Standard (mg/L)
0.0	0.0
0.20	0.02
0.50	0.05
1.00	0.10
2.50	0.25
5.00	0.50
10.0	1.0

2.8.7 Nitrite Standard, 1.0 mg/L: Add 0.1 mL of Stock Nitrite Solution (Section 2.8.3) to a 100 mL volumetric flask and dilute to volume with distilled water. Prepare fresh daily.

3.0 SAMPLE HANDLING AND PRESERVATION

3.1 Sampling procedure - Samples should be placed on ice and delivered to the laboratory as soon as possible.

3.2 Containers - Sampling containers used for this method are 1 L plastic cubitainers.

3.3 Storage conditions - Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4°C.

3.4 Holding Time Limits - Water samples preserved by chilling have a holding time of 48 hours; samples preserved with sulfuric acid (pH <2) have a holding time of 28 days. If nitrite is to be determined, samples must not be preserved and there is only a 48 hour holding time from time of sampling to time of analysis.

3.5 Solution Verification - Calibration solutions are verified with analysis of daily control spikes and references. Spiking solutions are prepared monthly and are verified prior to use by comparison to the calibration standards. All standard and spike solutions are maintained at 4°C.

4.0 CALIBRATION

4.1 Initial Calibration

The instrument is standardized by analyzing the calibration standards specified in Section 2.8.6 and a blank. The absorbance is read at 520 nm and the peak heights are read off the strip chart recorder. The linear regression equation is determined for concentration versus response. At least one nitrite standard should be compared to a nitrate standard at the same concentration to verify the efficiency of the reduction column. The efficiency must be at least 95 percent, or a new column must be prepared.

4.2 Calibration Checks

4.2.1 Calibration Check Standard - A Calibration Check standard (a known reference standard) must be analyzed after the calibration standards. The acceptance criteria of the Initial Calibration Check standard is ± 15 % of the known concentration.

4.2.2 Continuing Calibration Verification Standard - A Continuing Calibration Verification Standard (CCV) must be analyzed after every ten (10) samples and at the end of the analysis. The CCV is the 0.5 mg/L standard. The recovery based on the standard curve must be within 15 % of the known value.

4.2.3 If the recovery of the reference standard or CCV does not meet the acceptance criteria the reference standard or CCV must be rerun. If either reference standard or CCV still fails, the samples analyzed since the last acceptable reference or CCV standard must be rerun. If the samples are reanalyzed and the CCV still fails, then the Department Manager and the Laboratory Coordinator must be notified. The Laboratory Coordinator will notify USAEC to determine further action.

4.3 Daily Calibration

For daily calibration, an initial calibration curve and QC checks will be performed as indicated in Sections 4.1 and 4.2.

5.0 PROCEDURE

Daily control spike samples (Section 7.3) and environmental samples are prepared and analyzed as follows:

5.1 Separations - There is no separation stage in this method.

5.2 Chemical Reactions - Nitrate is reduced to nitrite by cadmium reduction column.

5.3 Instrument Analysis

5.3.1 Set up the Autoanalyzer II analytical cartridge, colorimeter, pump III, and sampler IV, according to configuration in Attachment A. Check pump tubing for wear and replace, if necessary.

5.3.2 With the reagent lines in Type I water, fasten the pump platen. Introduce the ammonium chloride-EDTA reagent and, after at least five minutes, place the cadmium reduction column in line, being careful not to introduce bubbles into the column. Wait ten minutes, then turn on the chart recorder. Set the colorimeter standard calibration knob to a reading of $\approx$ 50 and adjust the baseline control to obtain a chart reading of $\approx$ 2-5 chart units.

5.3.3 Condition the cadmium reduction column by sampling a cup of conditioning reagent (Section 2.6.4). Allow the instrument to equilibrate for at least twenty minutes before proceeding.

5.3.4 Prepare two sampling cups of 1.0 mg/L NO_3-N standard and one cup of 1.0 mg/L NO_2-N standard (Section 2.8.7). Analyze the three cups with the chart recorder adjusted to read ≈ 2-5 chart units. Adjust the standard calibration knob to obtain a chart reading of approximately 90% of full-scale when reading the first peak.

5.3.5 Compare the response of the second peak (NO_3) to the third peak (NO_2). A NO_3 peak of less than 95% of the height of the NO_2 peak indicates poor reduction efficiency. If necessary, recondition the column (Section 2.6.7) and repeat the reduction efficiency check.

5.3.6 Analyze the calibration standards in order of increasing concentration. Place a Type I water wash cup between each sample cup.

5.3.7 Analyze the daily quality control samples and reference sample.

5.3.8 Analyze the samples. Be sure to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) after every 10 samples.

Note: Preserved samples must be pH adjusted between pH 6 and pH 9 with NaOH prior to analysis.

5.3.9 Dilute samples that have concentrations exceeding the upper standard range and reanalyze.

5.3.10 End the run with a CCV and CCB to ensure that instruments have maintained stability throughout the run.

6.0 CALCULATION

6.1 Measure the peak height of each of the calibration standards and develop a linear regression fit for the standards by relating concentration to peak height. Verify that the correlation coefficient is ≥ 0.995 for the regression equation.

6.2 Use the linear regression equation, developed in Section 6.1, to the peak heights obtained for the samples and quality control standards to determine the concentration of nitrate + nitrite.

6.3 The sample concentration obtained from the curve must be multiplied by any dilution factors. Report results in mg/L.

7.0 DAILY QUALITY CONTROL

7.1 A Method blank (MB) must be analyzed with every lot. The MB consists of Type I water. Follow the same procedure as the samples.

7.2 A Continuing Calibration Blank (CCB) must be analyzed after every 10 samples. The CCB consists of Type I water.

7.3 The daily control spike samples are prepared by adding the following volumes of the Intermediate Nitrate Control Solution (Section 2.8.5) to 100 mL of Type I water.

Daily Control Spike Sample Prepared	Volume (mL) of AEC Intermediate Spike Solution	Concentration of Control Spike in Water (mg/L)
Blank	0	0
Low	0.4	0.04
High	4.0	0.4
High	4.0	0.4

7.4 The Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) are not required for AEC projects, but will be analyzed if required by the contract or project. If required, add 1.0 mL of the Intermediate Nitrate Control Solution (Section 2.8.5) to 1.0 mL of sample. Follow the same procedure as the samples.

7.5 Control Charts

7.5.1 Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control. Control charts are prepared for each target analyte using percent recovery data from the spiked QC samples (low and high level).

$$\% \text{ Recovery} = \frac{\text{Found Concentration - Method Blank}}{\text{Spiked Concentration}} \times 100$$

7.5.2 To prepare control charts, the analyst will submit a data batch including spike and method blank samples to Information Services after analysis. Information Services will put the information into the USAEC control chart program. The following control charts will be returned to the analysts.

7.5.2.1 Average (x) percent recovery for the two high concentration spiked QC samples in each lot,

7.5.2.2 Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,

7.5.2.3 Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and

7.5.2.4 Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

7.5.3 The average (x), average range (R) and control limits for x and R shall be updated after each lot for the first 20 in control lots. Limits established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 in control lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

8.0 REFERENCES

Methods for Chemical Analysis of Water and Wastes (EPA Method 353.2), EPA-600/4-79-020, Revised March 1983.

9.0 ATTACHMENTS

9.1 Attachment A - NITRATE + NITRITE MANIFOLD

9.2 Attachment B - TYPICAL TECHNICON RUN SEQUENCE

9.3 Attachment C - METHOD DETECTION LIMIT STUDY

Attachment A - Nitrate + Nitrite Manifold

Attachment B - TYPICAL TECHNICON RUN SEQUENCE

Calibration Standard (1.0 mg/L)	
Calibration Standard (1.0 mg/L)	
Cadmium Column Efficiency Check - NO_2 standard (1.0 mg/L)	
Blank	
Standard 1 (MDL)	
Standard 2	
Standard 3	
Standard 4	
Standard 5	
Standard 6	
Initial calibration blank	
Initial calibration verification - ICV (reference)	± 15 %
Method blank (prep blank)	
Low Spike - SP1	
High Spike - SP2	
High Spike - SP3	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike duplicate	
Sample #2	
Sample #3	
Sample #4	
Continuing calibration blank - CCB	
Continuing calibration verification - CCV	± 15%
Sample #5	
.	
.	
.	
Sample #14	
CCB	
CCV	± 15%
Sample #15	
.	
.	
.	
Sample #24	
CCB	
CCV	± 15%

Attachment C - METHOD DETECTION LIMIT STUDY

January 21, 1994

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

DETERMINATION OF NITRATE + NITRITE IN SOIL BY TECHNICON (MODIFIED EPA METHOD 353.2) USAEC METHOD - ANA2 - SOIL

TABLE OF CONTENTS

TITLE: DETERMINATION OF NITRATE + NITRITE IN SOIL BY TECHNICON (MODIFIED EPA METHOD 353.2)
USAEC METHOD - ANA2 - SOIL

1.0 SCOPE AND APPLICATION

1.1 Analytes

1.1.1 This ESE Standard Operating Procedure (SOP) follows EPA 353.2 protocols with additional quality control requirements applicable for the Class 1 analysis under United States Army Environmental Center (USAEC) guidelines for implementation of ER1110-1-263.

1.1.2 This SOP is applicable to the quantitative determination of nitrate + nitrite in soil samples.

1.2 Reporting Limits, Lower and Upper Standard Range and Chemical Abstract Service (CAS) Numbers

The reporting limits, lower and upper standard range and CAS number are:

Parameter	Reporting Limit (ug/g)	Lower Standard Range (mg/L)	Upper Standard Range (mg/L)	CAS Number
Nitrate + Nitrite	0.2	0.02	1.0	*

* There is no CAS Number for Nitrate + Nitrite.

1.3 Analysis Rate

After instrument calibration, one analyst can analyze approximately 20 soil samples in an 8-hour day.

1.4 Safety Information

General laboratory safety applies. Proper laboratory apparel must be worn at all times.

1.5 Summary of Method

Two grams of soil sample and 20 mL of sodium bicarbonate/sodium carbonate solution are shaken for 30 minutes. The mixture is centrifuged and the leachate is filtered through a 0.45 um filter. The sample is analyzed using an AutoAnalyzer with a nitrate cartridge equipped with a cadmium reduction column. Nitrate is reduced to nitrite in a cadmium reduction column, then nitrite is measured by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a colored azo dye.

1.6 Method Interferences

1.6.1 Suspended matter in the samples can accumulate in the cadmium column and restrict flow. Since nitrate and nitrite are highly soluble in water, samples may be pre-filtered to remove suspended particulates.

1.6.2 High concentrations of iron, copper or other metals may produce low results. EDTA added to the samples can help to reduce this interference.

1.6.3 Sulfides adversely affect the performance of the cadmium column, producing low results.

1.6.4 The presence of oil or grease in a sample can produce low results by coating the surface of the cadmium granules and interfering with nitrite reduction.

2.0 APPARATUS AND MATERIALS

2.1 Technicon AutoAnalyzer II, consisting of the following:

2.1.1 Sampler IV: with 30/hour, 2/1 sample/wash ratio cam.

2.1.2 Proportioning Pump.

2.1.3 Nitrate Analytical Cartridge.

2.1.4 Colorimeter equipped with a 15 millimeter flowcell and 520 nanometer filters.

2.1.5 Strip-chart recorder.

2.2 Filtering apparatus.

2.3 Millipore or equivalent membrane filters, 0.45 micrometers (um).

2.4 AutoAnalyzer sample cups (disposable).

2.5 Assorted Class A volumetric flasks and pipettes.

2.6 50 mL screw cap centrifuge tubes.

2.7 Reagents

2.7.1 Ammonium Chloride-EDTA Reagent: Dissolve 85 g of reagent NH_4Cl and 0.10 g disodium ethylenediamine tetraacetate in approximately 800 mL of Type I water. Adjust pH to 8.5 by adding approximately 7.0 mL 1O N NaOH and dilute to 1 liter. Add 0.5 mL Brij-35. Prepare fresh every 2 months.

2.7.2 Color Reagent: Add 40.0 g sulfanilamide, 2.0 g N-1-napthylethylenediamine dihydrochloride, 1 mL Brij-35, and 100 mL concentrated phosphoric acid to approximately 800 mL Type I water. Dissolve completely and dilute to 1 liter. Store in a dark bottle. This solution is stable for 2 months.

2.7.3 Wash solution: Add 0.5 mL Brij-35 to 1 liter Type I water.

2.7.4 Conditioning Reagent (for cadmium column): Dissolve 22.0 g ammonium chloride, 15.0 g cupric sulfate ($CuSO_4 \cdot 5H_2O$) and 1.0 g

EDTA in Type I water. Add 2.0 mL of 1000 mg/L Nitrate Stock Solution and dilute to 1 liter. Prepare fresh every 6 months.

2.7.5 Hydrochloric Acid (HCL) 1+1: Add 50 mL of concentrated HCL to a 100 mL volumetric flask and dilute to volume with Type I water.

2.7.6 Concentrate Eluent solution, 0.6 mM sodium bicarbonate/1.76 mM sodium carbonate: Dissolve 12.6 g of sodium bicarbonate and 46.64 g of sodium carbonate in reagent water and dilute to 2 liters.

2.7.7 Working Eluent solution: Dilute 16 mL of the Stock Eluent (Section 2.7.6) to 2 liters with reagent water.

2.7.8 Granulated cadmium, 40-60 mesh - Purchased from Alpkem Corporation. The cadmium granules (new or used) are cleaned with 1+1 HCl and copperized in the following fashion:

Place cadmium granules in a small beaker and add approximately 25 mL of 1+1 HCl. Swirl granules in a sonication bath until they appear silver.Decant the HCl solution and rinse thoroughly with approximately 500 mL of Type I water. Decant the Type I water and add 50 mL of conditioning reagent (Section 2.7.4). Swirl gently for 2 minutes, being careful not to expose the cadmium granules to air. Decant and repeat with another portion of conditioning reagent. Continue in this fashion until a brown colloidal precipitate just begins to form. The cadmium granules should appear black. Immediately decant all but about 10 mL of the solution and add approximately 50 mL of Type I water.

2.8 Preparation of reduction column

2.8.1 Place a glass wool plug in one end of a purple/black (P/N 116-0549P16) pump tube. Fill the tube with solution from the beaker which contains the prepared cadmium. Clamp off the end of the tube containing the glass wool plug.

2.8.2 Cut the end off of a blue Eppendorf pipet tip equal the inside diameter of the tube and push it into the end of the pump tube opposite the glass wool plug.

2.8.3 Using a small scoop, start to fill the column, adding a few granules at a time. Roll the column between the fingers to aid in filling the column and to dislodge granules caught in the tube. Fill to within 1/4 of an inch of the top of the tube.

2.8.4 The cadmium column is now complete and may be stored until needed by fastening both ends of the column together with a plastic nipple. Avoid allowing any air to enter the column.

2.9 Stock and Calibration Standards

2.9.1 Stock Nitrate Solution, 1000 mg/L: Dissolve 7.2182 g anhydrous potassium nitrate, oven dried at 110° C for 1 hour, in approximately 500 mL of Type I water and dilute to 1 liter. Store at 4° C. This solution is stable for 6 months.

2.9.2 Nitrate Control Stock, 1000 mg/L: Dissolve 6.0681 g anhydrous sodium nitrate, oven dried at 110°C for 1 hour, in approximately 500 mL of Type I water and dilute to 1 liter. Store at 4° C. This solution is stable for 6 months.

2.9.3 Stock Nitrite Solution, 1000 mg/L: Dissolve 6.072 g anhydrous potassium nitrite (stored in a desiccator) in approximately 500 mL of distilled water and dilute to volume. Store at 4° C. This solution is not stable, prepare fresh daily.

2.9.4 Intermediate Nitrate Standard, 10 mg/L: Add 1.0 mL of Stock Nitrate Solution (Section 2.9.1) to a 100 mL volumetric flask and dilute to volume with distilled water. Prepare fresh weekly.

2.9.5 Intermediate Nitrate Control, 10 mg/L: Add 1.0 mL of Nitrate Control Stock (Section 2.9.2) to a 100 mL volumetric flask and dilute to volume with Type I water. Prepare fresh each week.

2.9.6 Working Standards: The following dilution scheme can be used to prepare the calibration standards by adding the Intermediate Nitrate Standard (Section 2.9.4) to a 100 mL of Type I water. Prepare fresh each week.

Volume of Intermediate Nitrate Standard (mL)	Concentration of Nitrate Standard (mg/L)
0.0	0.0
0.20	0.02
0.50	0.05
1.00	0.10
2.50	0.25
5.00	0.50
10.0	1.0

2.9.7 Nitrite Standard, 1.0 mg/L: Add 0.1 mL of Stock Nitrite Solution (Section 2.9.3) to a 100 mL volumetric flask and dilute to volume with distilled water. Prepare fresh daily.

3.0 SAMPLE HANDLING AND PRESERVATION

3.1 Sampling procedure - Samples should be placed on ice and delivered to the laboratory as soon as possible.

3.2 Containers - Sampling containers used for this method are 500 mL wide-mouthed glass bottle.

3.3 Storage conditions - Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4°C.

3.4 Holding Time Limits - Samples stored at 4°C have a holding time of 28 days. Following leaching, analysis should occur within 48 hours unless, the leachate is preserved with H_2SO_4 to pH <2.

3.5 Solution Verification - Calibration solutions are verified with analysis of daily control spikes and references. Spiking solutions are prepared monthly and are

verified prior to use by comparison to the calibration standards. All standard and spike solutions are maintained at 4°C.

4.0 CALIBRATION

4.1 Initial Calibration

The instrument is standardized by analyzing the calibration standards specified in Section 2.9.6 and a blank. The absorbance is read at 520 nm and the peak heights are read off the strip chart recorder. The linear regression equation is determined for concentration versus response. At least one nitrite standard should be compared to a nitrate standard at the same concentration to verify the efficiency of the reduction column.

4.2 Calibration Checks

4.2.1 Calibration Check Standard - A Calibration Check standard (a known reference standard) must be analyzed after the calibration standards. The acceptance criteria of the Initial Calibration Check standard is ± 15 % of the known concentration.

4.2.2 Continuing Calibration Verification Standard - A Continuing Calibration Verification Standard (CCV) must be analyzed after every ten (10) samples and at the end of the analysis. The CCV is the 0.5 mg/L standard. The recovery based on the standard curve must be within 15 % of the known value.

4.2.3 If the recovery of the reference standard or CCV does not meet the acceptance criteria the reference standard or CCV must be rerun. If either reference standard or CCV still fails, the samples analyzed since the last acceptable reference or CCV standard must be rerun. If the samples are reanalyzed and the CCV still fails, then your Department Manager and the Laboratory Coordinator must be notified. The Laboratory Coordinator will notify USACE to determine further action.

4.3 Daily Calibration

For daily calibration, an initial calibration curve and QC checks will be performed as indicated in Sections 4.1 and 4.2.

5.0 PROCEDURE

Daily control spike samples (Section 7.3) and environmental samples are prepared and analyzed as follows:

5.1 Separations - The following extraction should be used for solid materials. Add 2.0 g of soil to a 50-mL, screw-cap centrifuge tube. All samples are analyzed as received and are not air dried or sieved. Add 20 mL of working eluent (Section 2.7.7) to the tubes. Prepare a method blank by placing 2 g of AEC standard soil and 20 mL of the working eluent into a centrifuge tube. Shake all tubes for 30 min. Centrifuge the tubes for 15 min. Decant a 2-3 mL aliquot of the sample into a sample cup. All samples are filtered through a 0.45-um filter prior to analysis.

5.2 Chemical Reactions - Nitrate is reduced to nitrite by a cadmium reduction column.

5.3 Instrument Analysis

5.3.1 Set up the Autoanalyzer II analytical cartridge, colorimeter, pump III, and sampler IV, according to configuration in Attachment A. Check pump tubing for wear and replace, if necessary.

5.3.2 With the reagent lines in Type I water, fasten the pump platen. Introduce the ammonium chloride-EDTA reagent and, after at least five minutes, place the cadmium reduction column in line, being careful not to introduce bubbles into the column. Wait ten minutes, then turn on the chart recorder. Set the colorimeter standard calibration knob to a reading of $\approx$ 50 and adjust the baseline control to obtain a chart reading of $\approx$ 2-5 chart units.

5.3.3 Condition the cadmium reduction column by sampling a cup of conditioning reagent (Section 2.7.4). Allow the instrument to equilibrate for at least twenty minutes before proceeding.

5.3.4 Prepare two sampling cups of 1.0 mg/L NO_3-N standard and one cup of 1.0 mg/L NO_2-N standard (Section 2.9.7). Analyze the three cups with the chart recorder adjusted to read $\approx$ 2-5 chart units. Adjust the standard calibration knob to obtain a chart reading of approximately 90% of full-scale when reading the first peak.

5.3.5 Compare the response of the second peak (NO_3) to the third peak (NO_2). A NO_3 peak of less than 95% of the height of the NO_2 peak indicates poor reduction efficiency. If necessary, recondition the column (Section 2.7.7) and repeat the reduction efficiency check.

5.3.6 Analyze the calibration standards in order of increasing concentration.

5.3.7 Analyze the daily quality control samples and reference sample.

5.3.8 Screen the samples for high levels of nitrate by the screening procedure outlined in Attachment E. Analyze the samples. Be sure to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) after every 10 samples.

5.3.9 Dilute samples that have concentrations exceeding the upper standard range and reanalyze.

5.3.10 End the run with a CCV and CCB to ensure that instruments have maintained stability throughout the run.

6.0 CALCULATION

6.1 Measure the peak height of each of the calibration standards and develop a linear regression fit for the standards by relating concentration to peak height. Verify that the correlation coefficient is $\geq$ 0.995 for the regression equation.

6.2 Use the linear regression equation, developed in Section 6.1, to the peak heights obtained for the samples and quality control standards to determine the concentration of nitrate + nitrite.

6.3 To determine the concentration of nitrate + nitrite in the original sample the following example equation should be used:

$$\text{Sample conc. (ug/g)} = \frac{\text{Curve conc. x Dilution Factor x Final Extract Volume}}{\text{Sample Weight x \% moisture}}$$

7.0 DAILY QUALITY CONTROL

7.1 A Method blank (MB) must be extracted and analyzed with every lot. The MB consists of 2 g of AEC standard soil. Follow the same procedure as the samples.

7.2 A Continuing Calibration Blank (CCB) must be analyzed after every 10 samples. The CCB consists of Type I water.

7.3 The daily control spike samples are prepared by adding the following volumes of the Intermediate Nitrate Control Solution (Section 2.9.5) to 2.0 g of AEC standard soil. Allow spike sample to equilibrate for 1 hour before extracting.

Daily Control Spike Sample Prepared	Volume (mL) of AEC Intermediate Spike Solution	Concentration of Control Spike in Soil (ug/g)
Blank	0	0
Low	0.08	0.4
High	0.8	4.0
High	0.8	4.0

7.4 The Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) are not required for AEC projects, but will be analyzed if required by the

contract or project. If required, add 1.0 mL of the Intermediate Nitrate Control Solution (Section 2.9.5) to 2.0 g of soil sample. Allow spike sample to equilibrate for 1 hour before extracting. Follow the same procedure as the samples.

7.5 Control Charts

7.5.1 Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control. Control charts are prepared for each target analyte using percent recovery data from the spiked QC samples (low and high level).

$$\% \text{ Recovery} = \frac{\text{Found Concentration - Method Blank}}{\text{Spiked Concentration}} \times 100$$

7.5.2 To prepare control charts, the analyst will submit a data batch including spike and method blank samples to Information Services after analysis. Information Services will put the information into the USAEC control chart program. The following control charts will be returned to the analysts.

7.5.2.1 Average (x) percent recovery for the two high concentration spiked QC samples in each lot,

7.5.2.2 Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,

7.5.2.3 Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and

7.5.2.4 Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

7.5.3 The average (x), average range (R) and control limits for x and R shall be updated after each lot for the first 20 in control lots. Limits established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 in control lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

8.0 REFERENCES

Methods for Chemical Analysis of Water and Wastes (EPA Method 353.2), EPA-600/4-79-020, Revised March 1983.

9.0 ATTACHMENTS

9.1 Attachment A - **NITRATE + NITRITE MANIFOLD**

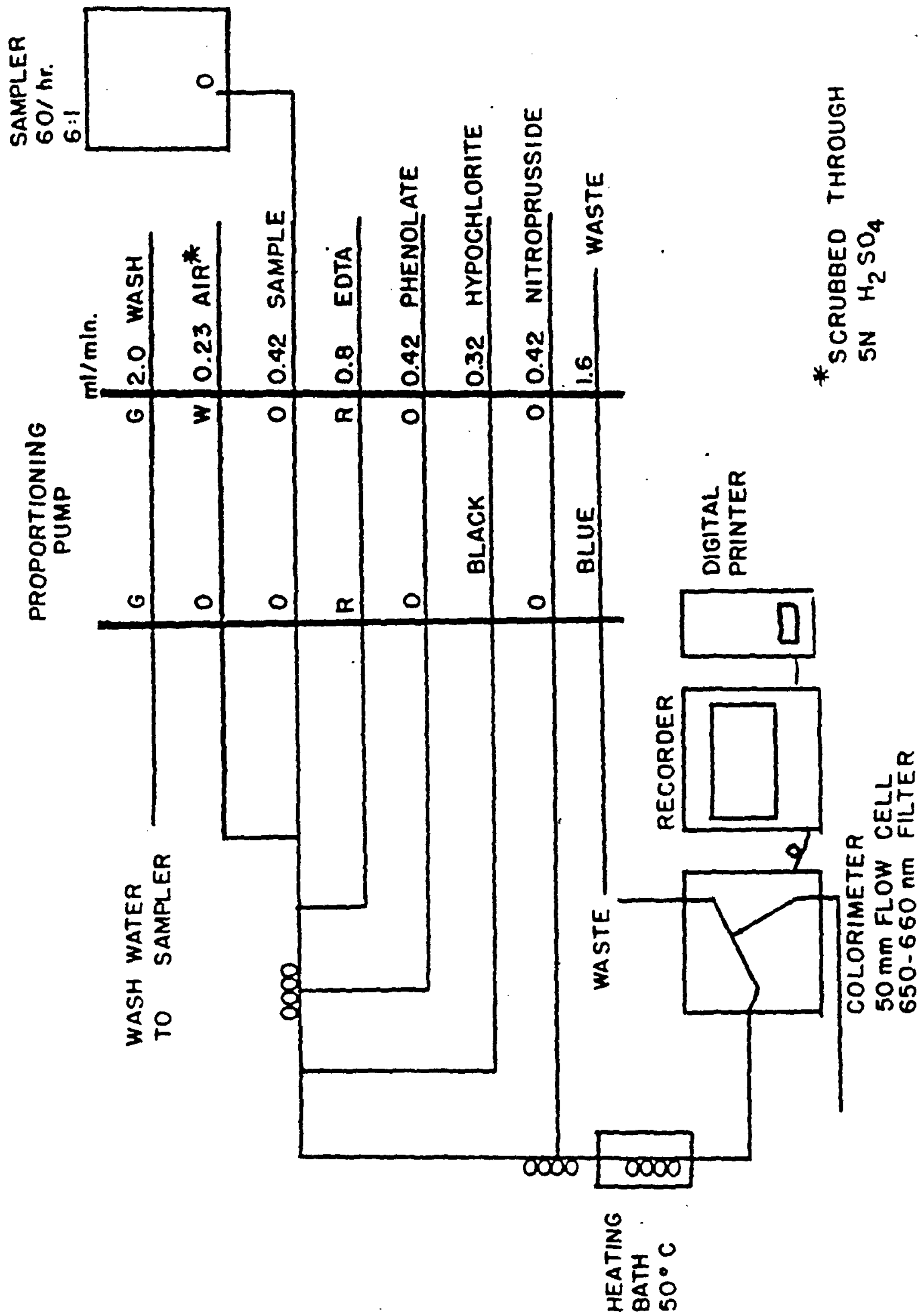
9.2 Attachment B - **TYPICAL TECHNICON RUN SEQUENCE**

9.3 Attachment C - **METHOD DETECTION LIMIT STUDY**

9.4 Attachment D - **DEVIATION FROM METHOD 353.2**

9.5 Attachment E - **NITRATE / NITRITE SCREENING PROCEDURE**

Attachment A - AMMONIA MANIFOLD



October 27, 1993

Attachment B - **TYPICAL TECHNICON RUN SEQUENCE**

Calibration Standard (1.0 mg/L)	
Calibration Standard (1.0 mg/L)	
Cadmium Column Efficiency Check - NO_2 standard (1.0 mg/L)	
Blank	
Standard 1 (MDL)	
Standard 2	
Standard 3	
Standard 4	
Standard 5	
Standard 6	
Initial calibration blank	
Initial calibration verification - ICV (reference)	± 15 %
Method blank (prep blank)	
Low Spike - SP1	
High Spike - SP2	
High Spike - SP3	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike duplicate	
Sample #2	
Sample #3	
Sample #4	
Continuing calibration blank - CCB	
Continuing calibration verification - CCV	± 15%
Sample #5	
.	
.	
.	
Sample #14	
CCB	
CCV	± 15%
Sample #15	
.	
.	
.	
Sample #24	
CCB	
CCV	± 15%

Attachment C - METHOD DETECTION LIMIT STUDY

METHOD DETECTION LIMIT STUDY

Laboratory Name: Environmental Science & Engineering, Inc. (ESE)
Address: P.O. Box 1703, Gainesville, Florida, 32602-1703
Manager: Dr. John J. Mousa, Director, Gainesville Laboratory
Phone: (904) 332-3318

Method: Nitrate + Nitrite in Soil (Modified EPA Method 353.2/KT05)

Compound Name	R1 (mg/kg)	R2 (mg/kg)	R3 (mg/kg)	R4 (mg/kg)	R5 (mg/kg)	R6 (mg/kg)	R7 (mg/kg)	X (mg/kg)	S	MDL (mg/kg)
Nitrate + Nitrite	0.890	0.900	0.890	0.890	0.900	0.910	0.890	0.896	0.007	0.025

Note: Nitrate + Nitrite target concentration is 1.0 mg/kg

R = Actual concentration for each replicate 1-7
X = Average concentration
S = Standard deviation
mg/kg = milligrams per kilogram

October 27, 1993

Attachment D - DEVIATION FROM METHOD 353.2

1. Soil and sediment matrices are not included in the scope of EPA Method 353.2. Therefore, EPA Method 353.2 has been modified for inclusion of soil and sediment samples in the method. Appropriate method detection limit studies support the applicability of this method to soil and sediment matrices. The modifications made are as follows:

    Two grams of a soil sample are used in place of an aliquot of the water sample.

    Twenty mL of the eluent are added to the soil sample to leach nitrate and nitrite from the soil.

    The soil sample is shaken for 30 minutes and then centrifuged for 15 min. A 2-3 mL aliquot of the sample is decanted into a sample cup.

    Samples are analyzed as defined in EPA Method 353.2 with no further deviations.

Attachment E - **NITRATE/NITRITE SCREENING PROCEDURE**

E.1 Screen each sample with NO_3-Merckoquant® Nitrate test strips to determine which samples may cause the instrument to overload. All samples should be analyzed undiluted unless the nitrate/nitrite screen indicates a significantly high level.

E.2 Read the instruction brochure supplied by the manufacturer.

E.3 Use the decanted extract to determine the nitrate/nitrite content.

E.4 Do not touch the two reaction zones on the test strip.

E.5 Place an aliquot of extract onto the test strip, saturating the reaction zones.

E.6 Note the color change and estimate the level of nitrate/nitrite in the sample.

E.7 Dilute the sample accordingly and analyze. The sample concentration should ideally be diluted into the upper 2/3 of the calibration curve.

E.8 Unopened NO_3-Merckoquant® Nitrate test strips should be stored in the refrigerator. Opened packs should be stored as dry and cool as possible, but <u>not</u> in the refrigerator because the condensed moisture from the atmosphere will exceed the capacity of the drying agent in the package.

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

DETERMINATION OF INORGANIC ANIONS IN WATER BY ION CHROMATOGRAPHY (EPA METHOD 300.0) USAEC METHOD - ANI1 - WATER

TABLE OF CONTENTS

TITLE: DETERMINATION OF INORGANIC ANIONS IN WATER BY ION CHROMATOGRAPHY (EPA METHOD 300.0) USAEC METHOD - ANI1 -WATER

1.0 SCOPE AND APPLICATION

1.1 Analytes

1.1.1 This ESE standard operating procedure (SOP) follows EPA 300.0 protocols with additional quality control requirements applicable for the Class 1 analysis under United States Army Environmental Center (USAEC) guidelines for implementation of ER1110-1-263.

1.1.2 This method is applicable to the quantitative determination of fluoride, chloride, bromide, and sulfate in water samples.

1.2 Matrix

This method is applicable to all environmental water matrices.

1.3 Reporting Limit, Lower and Upper Standard Range, and Chemical Abstract Service (CAS) Number

The reporting limits, the lower and upper standard ranges, and CAS numbers are:

Parameter	Reporting Limit (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)	CAS Number
Fluoride (F)	500	500	30,000	16984-48-8
Chloride (Cl)	500	500	30,000	16887-00-6
Bromide (Br)	5000	1000	30,000	24959-67-9
Sulfate (SO4)	5000	5000	300,000	14808-79-8

1.4 Analysis Rate

An analyst can prepare and analyze 20 samples per 8 hour day.

1.5 Safety Information

Normal laboratory safety practices should be employed during the performance of this analysis. No special precautions are required unless the samples are hazardous.

1.6 Summary of Method

A water sample is injected into a stream of carbonate-bicarbonate eluant and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affinities for a low capacity and strongly basic anion exchanger (guard and separator column). The separated anions are directed onto a strongly acidic cation exchanger (suppressor column) where they are converted to their highly conductive acid form and the carbonate-bicarbonate eluant is converted to a weakly conductive carbonic acid. The now separated anions, each in their acid form, are measured by conductivity. They are identified on the basis of retention time compared to standards. Quantitation is performed by measurement of peak area when using the Maxima® integration system and peak height when using the 1-volt input strip chart recorder.

1.7 Method Interferences

1.7.1 Interferences can be caused by substances with retention times that are similar to and overlap with those of the anion(s) of interest. Large amounts of anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

1.7.2 The water dip or negative peak that elutes near and which interferes with the fluoride peak can be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (Section 2.4.5) to 100 mL of each standard and sample.

1.7.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware or other sample processing accessories that lead to discrete artifacts or an elevated baseline in ion chromatograms.

1.7.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

1.7.5 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and will interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy in each sample matrix.

1.7.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

2.0 APPARATUS AND MATERIALS

2.1 Glassware/Hardware

2.1.1 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

2.1.2 Class A volumetric flasks - 1 and 2 liter and 200 mL.

2.1.3 Class A volumetric pipets - various sizes.

2.2. Instrumentation

2.2.1 A Dionex 2120i Ion Chromatograph with an autosampler and a 1-volt input strip chart recorder with the following columns:

2.2.1.1 Anion guard column: Dionex high-pressure liquid chromatograph (HPLC) AG4A;

2.2.1.2 Anion separator column: Dionex HPLC AS-4A;

2.2.1.3 Anion suppressor column: AMMS-II P/N 023074;

2.2.1.4 Flow rate and pressure: 2.0 milliliters per minute (mL/min) at 550 to 750 pounds per square inch (psi);

2.2.1.5 Detector range: 100 microSiemens (uS) full scale;

2.2.1.6 Sample loop: 50 microliter (uL) will be used.

2.2.2 A Dionex 2120i Ion Chromatograph with an autosampler and Maxima® integration system with the following columns:

2.2.2.1 Anion guard column: Dionex high-pressure liquid chromatograph (HPLC) AG4A;

2.2.2.2 Anion separator column: Dionex HPLC AS-4A;

2.2.2.3 Anion suppressor column: AMMS-II P/N 043074;

2.2.2.4 Flow rate and pressure: 2.0 milliliters per minute (mL/min) at 550 to 750 pounds per square inch (psi);

2.2.2.5 Detector range: 100 microSiemens (uS) full scale;

2.2.2.6 Sample loop: 50 microliter (uL) will be used.

2.2.3 A Dionex 4000i Ion Chromatograph with an autosampler and Maxima® integration system with the following columns:

2.2.3.1 Anion guard column: Dionex high-pressure liquid chromatograph (HPLC) AG4A;

2.2.3.2	Anion separator column:	Dionex HPLC AS-4A;
2.2.3.3	Anion suppressor column:	AMMS-II P/N 043074;
2.2.3.4	Flow rate and pressure:	2.0 milliliters per minute (mL/min) at 550 to 750 pounds per square inch (psi);
2.2.3.5	Detector range:	100 microSiemens (uS) full scale;
2.2.3.6	Sample loop:	50 microliter (uL) will be used.

2.3 Retention Time Criteria

2.3.1 Retention times using a strip chart recorder - Retention times are established from the results of the midlevel standard (Standard C). The instrument marks on the chart paper when the sample or standard is injected (zero time). The sample chart is placed on top of the standard C chart. The zero time mark is used to line up the standard and sample charts. The sample chart is then compared to the standard chart. A retention time window of ± 1 mm is used. If there are peaks near the retention window, a sample of a lot of 20 samples is chosen and spiked to verify the analyte identity. Spikes will be prepared by diluting the sample 1:1 with the high spike standard spike solution (Section 7.3)

2.3.2 Retention times using the Maxima® integration system - Retention times are established from the results of the high level standard (Standard H). Retention time windows for the four analytes will be as follows:

Fluoride and Chloride	± 0.16 minutes
Bromide and Sulfate	± 0.30 minutes

Retention times are verified when the Continuing Calibration Verification (CCV) is analyzed. If the CCV retention times show shifting, then one sample will be spiked to verify analyte identify. Spikes will be prepared by diluting the sample 1:1 with the high spike standard spike solution (Section 7.3)

2.4 Reagents

2.4.1 Sulfuric Acid (H_2SO_4), ACS grade.

2.4.2 Sodium bicarbonate ($NaHCO_3$), ACS grade.

2.4.3 Sodium carbonate (Na_2CO_3), ACS grade.

2.4.4 Reagent water: Deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

2.4.5 Concentrate Eluent solution, 0.6 mM sodium bicarbonate/1.76 mM sodium carbonate: Dissolve 12.6 g of sodium bicarbonate and 46.64 g of sodium carbonate in reagent water and dilute to 2 liters.

2.4.6 Standard Eluent solution, 80%: Pipet 80 mL of the concentrate (Section 2.4.5) eluent solution into a 100 mL volumetric flask and dilute to volume with reagent water.

2.4.7 Working Eluent solution: Dilute 16 mL of the Stock Eluent (Section 2.4.5) to 2 liters with reagent water.

2.4.8 Regeneration solution (membrane suppressor): 0.025N Sulfuric acid. Dilute 10 mL 5 N sulfuric acid (H_2SO_4) to 2 liters with reagent water.

2.4.9 Preparation of Standards

2.4.9.1 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions are prepared from ACS reagent grade materials (dried at 110°C for 2 hr) as listed below.

2.4.9.1.1 Chloride (Cl^-) 1000 mg/L: Dissolve 1.6485 g of sodium chloride (NaCl) in reagent water and dilute to 1 liter.

2.4.9.1.2 Sulfate (SO_4^{-2}) 1000 mg/L: Dissolve 1.8141 g of potassium sulfate (K_2SO_4) in reagent water and dilute to 1 liter.

2.4.9.1.3 Bromide (Br^-) 1000 mg/L: Dissolve 1.2876 g of sodium bromide (NaBr) in reagent water and dilute to 1 liter.

2.4.9.1.4 Fluoride (F^-) 1000 mg/L: Dissolve 2.1000 g of sodium fluoride (NaF) in reagent water and dilute to 1 liter.

2.4.9.1.5 Stability of standards: Stock standards are stable for at least six months when stored at 4° C.

2.4.9.2 Combined Intermediate Standard - 50 mg/L Fluoride, Chloride and Bromide: Pipet 10 mL each of the Fluoride, Chloride and Bromide Stock standard into a 200 mL volumetric flask and dilute to volume with reagent water. Prepare fresh monthly.

2.4.9.3 Working Calibration Curve: Add the following volumes of the Combined Intermediate Standard (Section 2.4.9.2) and Stock Sulfate Standard (Section 2.4.9.1.2) to a 100 mL volumetric flask and dilute to volume. Add 1 ml of the standard eluent solution to each standard prior to diluting to volume. Prepare fresh weekly.

Prepared Calibration Standard	Volume (mL) of Combined Intermediate Standard	Volume (mL) of Sulfate Stock Standard	Concentration (ug/L)			
			F	Cl	Br	SO_4
Blank	0.0	0.0	0.0	0.0	0.0	0.0
A	1.0	0.5	500	500	500*	5,000
B	2.0	1.0	1,000	1,000	1,000	10,000
C	6.0	2.0	3,000	3,000	3,000	20,000
D	10.0	5.0	5,000	5,000	5,000	50,000
E	20.0	10.0	10,000	10,000	10,000	100,000
F	40.0	2.0	20,000	20,000	20,000	200,000
G	50.0	2.5	25,000	25,000	25,000	250,000
H	60.0	30.0	30,000	30,000	30,000	300,000

*Below the reporting limit of bromide and are not used in the calibration curve.

2.4.9.4 Control Stock Solution, 1000 mg/L: Prepared as specified under Stock Standard solutions (Section 2.4.9.1).

NOTE: It is recommended that these solid reagents be obtained from a different source supplier than the solid reagents used for making the Stock Standard Solution (Section 2.4.9.1). However, if the solid reagents to be used are obtained from the same manufacturer, it must be from a different lot than the Stock Standard Solution.

3.0 SAMPLE HANDLING AND STORAGE

3.1 Sampling Procedure - There are no special considerations required due to the nature of the anions. The samples need to be chilled to 4 °C immediately following sampling.

3.2 Containers - The sampling container used is a 1 L cubitainer.

3.3 Storage Conditions - Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4°C.

3.4 Holding Time Limits - The holding time for water samples is 28 days from the time of sampling to time of analysis.

3.5 Solution Verification - Calibration solutions are verified with the analysis of daily control spikes and reference samples. Daily control spikes are prepared by a combination of individual stocks and combined intermediate stocks. Since there is no extraction in this method, the analysis of the daily control spikes serve two purposes:

3.5.1 As verification of the spiking stock solutions and,

3.5.2 For method control chart plotting.

If daily control spikes are outside of control limits due to problems with the stock, the individual stocks and control spikes must be freshly prepared and analyzed before continuing analysis of the samples.

4.0 CALIBRATION

4.1 Initial Calibration

The instrument is standardized by analyzing the calibration standards as specified in Section 2.4.9.3 and a blank. The peak heights are read off the strip chart recorder and peak area are read off the Maxima® integration system. The best fit quadratic regression equation is determined for concentration versus response.

4.2 Calibration Checks

4.2.1 Calibration Check Standard - A Calibration Check standard (a known reference standard) must be analyzed after the calibration standards. The Calibration Check standard must contain all analytes of interest and the concentration must be near the upper range of the standard curve. (The purchased calibration check standard contains all analytes, except Br^-. The calibration check standard for Br^- is prepared separately.) The acceptance criteria of the Initial Calibration Check standard is ± 15 % of the known concentration.

4.2.2 Continuing Calibration Verification Standard - A Continuing Calibration Verification Standard (CCV) must be analyzed after every ten (10) samples and at the end of the analysis. The CCV is standard H. The recovery based on the standard curve must be within 10 % of the known value.

4.2.3 If the recovery of the reference standard or CCV does not meet the acceptance criteria the standard must be rerun. If either standard still fails, the samples analyzed since the last acceptable standard must be rerun. If the samples are reanalyzed and the CCV still fails, then your Department Manager and the Laboratory Coordinator must be notified. The Laboratory Coordinator will notify USACE to determine further action.

4.3 Daily Calibration

For daily calibration, an initial calibration curve and QC checks will be performed as indicated in Sections 4.1 and 4.2.

5.0 PROCEDURE

Daily control spike samples (Section 7.0) and environmental samples are prepared and analyzed as follows:

5.1 Separations - All samples are filtered through a 0.20-um frit that is in-line with the instrument prior to analysis.

5.2 Reactions - There are no chemical reaction steps.

5.3 Instrumental Analysis - The samples are analyzed on an Ion Chromatograph as follows (see Attachment A for a typical IC run sequence):

5.3.1 Establish a stable baseline by pumping the working eluent solution through the instrument for approximately 15 to 30 minutes.

5.3.2 Pour the daily calibration standards into the sample cups in ascending order, beginning with the highest standard to calibrate the instrument, then a blank and the remainder of the standards.

5.3.3. Pour the daily control spike samples and reference sample into the sample cups and analyze.

5.3.4. Pour the environmental samples into the sample cups and analyze.

5.3.5. Reanalyze Calibration Standard H after every ten (10) samples and at the end of the analytical run.

5.3.6. Dilute samples that have concentrations exceeding the upper standard range and reanalyze.

6.0 CALCULATION

6.1 Prepare separate calibration curves for each anion of interest. Plot the standard peak heights (if using strip chart recorder) or peak area (if using the Maxima® integration system) against concentration values and calculate the quadratic regression equation. Compute the sample concentration by using the quadratic regression equation.

6.2 Verify that the correlation coefficient of the curve is $\geq$ 0.995.

6.3 The sample concentration obtained from the curve must be multiplied by any dilution factors. Report results in mg/L.

7.0 DAILY QUALITY CONTROL

Quality control stock solutions obtained from an independent source are prepared as indicated in Section 2.4.9.4.

7.1. The low level spike is prepared by adding the following volumes of control stock standard to 100 mL of Type I water. Prepare the spike fresh monthly. Analyze using the same procedure as the samples.

Analyte	Volume (mL) of Control Stock Standard	Low Level Spike Target (ug/L)
Fluoride	0.1	1,000
Chloride	0.1	1,000
Bromide	1.0	10,000
Sulfate	1.0	10,000

7.2. The high level spike is prepared by adding the following volumes of control stock standard to 100 mL of Type I water. Prepare the spike fresh monthly. Analyze using the same procedure as the samples.

Analyte	Volume (mL) of Control Stock Standard	High Level Spike Target (ug/L)
Fluoride	1.0	10,000
Chloride	1.0	10,000
Bromide	5.0	50,000
Sulfate	10.0	100,000

7.3 A method blank (MB) must be analyzed for every lot of 20 samples. The Method Blank is Type I water. Follow the same procedure used for the samples.

7.4 A Continuing Calibration Blank (CCB) must be analyzed after every ten (10) samples. The CCB is prepared by adding 1 mL of eluent to 100 mL of Type I water.

7.5 The Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) are not required for AEC projects, but will be analyzed if required by the contract or project. If required, the SPM and SPMD are made by preparing a 1:1 dilution of the high spike solution and the sample. A SPM and SPMD will be analyzed with every lot of 20 samples. The spiking concentration must be within the concentration range of the calibration standards. The analyst may need to spike the dilution of a sample if interferences or high concentrations of the spike analytes cause an inaccurate calculation of the matrix spike recovery.

7.6 Control Charts

7.6.1 Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control. Control charts are prepared for each target analyte using percent recovery data from the spiked QC samples (low and high level).

$$\% \text{ Recovery} = \frac{\text{Found Concentration - Method Blank}}{\text{Spiked Concentration}} \times 100$$

7.6.2 To prepare control charts, the analyst will submit a data batch including spike and method blank samples to Information Services after analysis. Information Services will put the information into the USAEC control chart program. The following control charts will be returned to the analysts.

7.6.2.1 Average (x) percent recovery for the two high concentration spiked QC samples in each lot,

7.6.2.2 Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,

7.6.2.3 Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and

7.6.2.4 Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

7.6.3 The average (x), average range (R) and control limits for x and R shall be updated after each lot for the first 20 in control lots. Limits established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 in control lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

8.0 REFERENCES

8.1 Dionex Instrument Operation Manual.

8.2 U.S. Environmental Protection Agency (EPA) Test Method 300.0 (EPA-600/4-84-017).

9.0 ATTACHMENT

9.1 Attachment A - **TYPICAL ION CHROMATOGRAPH RUN SEQUENCE**

9.2 Attachment B - **METHOD DETECTION STUDY**

9.3 Attachment C - **DEVIATIONS FROM EPA METHOD 300.0**

Attachment A - TYPICAL ION CHROMATOGRAPH RUN SEQUENCE

High standard to check instrument range	
Blank	
Standard 1 (MDL)	
Standard 2	
Standard 3	
Standard 4	
Standard 5	
Standard 6	
Standard 7	
Standard 8	
Initial calibration verification - ICV (reference)	± 15
Method blank (prep blank)	
Low Spike - SP1	
High Spike - SP2	
High Spike - SP3	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike duplicate	
Sample #2	
Sample #3	
Continuing calibration blank - CCB	
Continuing calibration verification - CCV	± 15%
Sample #4	
.	
.	
.	
Sample #13	
CCB	
CCV	± 15%
Sample #14	
.	
.	
.	
Sample #20	
CCB	
CCV	± 15%

Attachment B - **METHOD DETECTION STUDY**

Attachment C - DEVIATIONS FROM EPA METHOD 300.0

1. The eluent solution (Section 2.4.7) is a lower concentration than indicated in the method. The lower concentration of eluent is used because it provides better separation between the analytes.

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

DETERMINATION OF INORGANIC ANIONS IN SOIL AND SEDIMENT BY ION CHROMATOGRAPHY (EPA METHOD 300.0)
USAEC METHOD - ANI1 - SOIL

TABLE OF CONTENTS

TITLE: **DETERMINATION OF INORGANIC ANIONS IN SOIL AND SEDIMENT BY ION CHROMATOGRAPHY (EPA METHOD 300.0) USAEC METHOD - ANI1 - SOIL**

1.0 SCOPE AND APPLICATION

1.1 Analytes

1.1.1 This ESE standard operating procedure (SOP) follows EPA 300.0 protocols with additional quality control requirements applicable for the Class 1 analysis under United States Army Environmental Center (USAEC) guidelines for implementation of ER1110-1-263.

1.1.2 This Standard Operating Procedure (SOP) is applicable to the quantitative determination of fluoride, chloride, bromide, and sulfate in soil samples.

1.2 Matrix

This method is applicable to all environmental soil and sediment samples.

1.3 Reporting Limit, Lower and Upper Standard Range and Chemical Abstract Service (CAS) Number

The reporting limits, the lower and upper standard range and CAS numbers are:

Analytes	Reporting Limits (ug/g)	Lower Standard Range (mg/L)	Upper Standard Range (mg/L)	CAS Number
Fluoride (F)	2.5	0.05	6.25	16984-48-8
Chloride (Cl)	5.0	0.1	12.5	16887-00-6
Bromide (Br)	10.0	1.0	25.0	24959-67-9
Sulfate (SO4)	25.0	0.5	62.5	14808-79-8

Note: Multiply standard by 10 to obtain upper range for method in ug/g unit.

1.4 Analysis Rate

An analyst can prepare and analyze 20 samples per 8-hour day.

1.5 Safety Information

Normal laboratory safety practices should be employed during the performance of this analysis. No special precautions are required unless the samples are hazardous.

1.6 Summary of Method

Two grams of a soil sample and 20 mL of the Ion Chromatographic eluent (sodium bicarbonate/sodium carbonate mixture) are shaken for 30 minutes. The mixture is centrifuged and the leachate is filtered through a 0.20-um in-line frit. The sample is injected into a stream of carbonate-bicarbonate eluant and passed through a series of ion exchangers. The anions of interest are separated on the basis of their relative affinities for a low capacity and strongly basic anion exchanger (guard and separator column). The separated anions are directed onto a strongly acidic cation exchanger (suppressor column) where they are converted to their highly conductive acid form and the carbonate-bicarbonate eluant is converted to a weakly conductive carbonic acid. The now separated anions, each in their acid form, are measured by conductivity. They are identified on the basis of retention time compared to standards. Quantitation is performed by measurement of peak area when using the Maxima® integration system and peak height when using the 1-volt input strip chart recorder.

1.7 Method Interferences

1.7.1 Interferences can be caused by substances with retention times that are similar to and overlap with those of the anion(s) of interest. Large amounts of anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

1.7.2 The water dip or negative peak that elutes near and which interferes with the fluoride peak can be eliminated by the addition of the

equivalent of 1 mL of concentrated eluent (Section 2.4.5) to 100 mL of each standard and sample.

1.7.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware or other sample processing accessories that lead to discrete artifacts or an elevated baseline in ion chromatograms.

1.7.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

1.7.5 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and will interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy in each sample matrix.

1.7.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

2.0 APPARATUS AND MATERIALS

2.1 Glassware/Hardware

2.1.1 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

2.1.2 Class A volumetric flasks - 1 and 2 liter and 200 mL.

2.1.3 Class A volumetric pipets - various sizes.

2.1.4 50 mL centrifuge tubes with screw caps.

2.1.5 Centrifuge.

2.2. Instrumentation

2.2.1 A Dionex 2120i Ion Chromatograph with an autosampler and a 1-volt input strip chart recorder with the following columns:

2.2.1.1	Anion guard column:	Dionex high-pressure liquid chromatograph (HPLC) AG4A;
2.2.1.2	Anion separator column:	Dionex HPLC AS-4A;
2.2.1.3	Anion suppressor column:	AMMS-II P/N 043074;
2.2.1.4	Flow rate and pressure:	2.0 milliliters per minute (mL/min) at 550 to 750 pounds per square inch (psi);
2.2.1.5	Detector range:	30 microSiemens (uS) full scale;
2.2.1.6	Sample loop:	50 microliter (uL) will be used.

2.2.2 A Dionex 2120i Ion Chromatograph with an autosampler and Maxima® integration system with the following columns:

2.2.2.1	Anion guard column:	Dionex high-pressure liquid chromatograph (HPLC) AG4A;
2.2.2.2	Anion separator column:	Dionex HPLC AS-4A;
2.2.2.3	Anion suppressor column:	AMMS-II P/N 043074;

2.2.2.4	Flow rate and pressure:	2.0 milliliters per minute (mL/min) at 550 to 750 pounds per square inch (psi);
2.2.2.5	Detector range:	30 microSiemens (uS) full scale;
2.2.2.6	Sample loop:	50 microliter (uL) will be used.

2.2.3 A Dionex 4000i Ion Chromatograph with an autosampler and Maxima® integration system with the following columns:

2.2.3.1	Anion guard column:	Dionex high-pressure liquid chromatograph (HPLC) AG4A;
2.2.3.2	Anion separator column:	Dionex HPLC AS-4A;
2.2.3.3	Anion suppressor column:	AMMS-II P/N 043074;
2.2.3.4	Flow rate and pressure:	2.0 milliliters per minute (mL/min) at 550 to 750 pounds per square inch (psi);
2.2.3.5	Detector range:	30 microSiemens (uS) full scale;
2.2.3.6	Sample loop:	50 microliter (uL) will be used.

2.3 Retention Time Criteria

2.3.1 Retention times using a strip chart recorder - Retention times are established from the results of the standard (Standard C). The instrument marks on the chart paper when the sample or standard is injected (zero time). The sample chart is placed on top of the standard C chart. The zero time mark is used to line up the standard and sample charts. The sample chart is then compared to the standard chart. A retention time window of $\pm$ 1 mm is used. If there are peaks near the retention window, a sample of a lot of 20 samples is chosen and spiked to verify the analyte identity. Spikes will be prepared by diluting the sample 1:1 with the high spike standard spike solution (Section 7.3)

2.3.2 Retention times using the Maxima® integration system - Retention times are established from the results of the high level standard (Standard H). Retention time windows for the four analytes will be as follows:

Fluoride and Chloride	$\pm$ 0.16 minutes
Bromide and Sulfate	$\pm$ 0.30 minutes

Retention times are verified when the Continuing Calibration Verification (CCV) is analyzed. If the CCV retention times show shifting, then one sample will be spiked to verify analyte identify. Spikes will be prepared by diluting the sample 1:1 with the high spike standard spike solution (Section 7.3)

2.4 Reagents

2.4.1 Sulfuric Acid (H_2SO_4), ACS grade.

2.4.2 Sodium bicarbonate ($NaHCO_3$), ACS grade.

2.4.3 Sodium carbonate (Na_2CO_3), ACS grade.

2.4.4 Reagent water: Deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

2.4.5 Concentrate Eluent solution, 0.6 mM sodium bicarbonate/1.76 mM sodium carbonate: Dissolve 12.6 g of sodium bicarbonate and 46.64 g of sodium carbonate in reagent water and dilute to 2 liters.

2.4.6 Standard Eluent solution, 80%: Pipet 80 mL of the concentrate (Section 2.4.5) eluent solution into a 100 mL volumetric flask and dilute to volume with reagent water.

2.4.7 Working Eluent solution: Dilute 16 mL of the Stock Eluent (Section 2.4.5) to 2 liters with reagent water.

2.4.8 Regeneration solution (membrane suppressor): 0.025N Sulfuric acid. Dilute 10 mL 5 N sulfuric acid (H_2SO_4) to 2 liters with reagent water.

2.4.9 Preparation of Standards

2.4.9.1 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions are prepared from ACS reagent grade materials (dried at 110°C for 2 hr) as listed below.

2.4.9.1.1 Chloride (Cl^-) 1000 mg/L: Dissolve 1.6485 g of sodium chloride (NaCl) in reagent water and dilute to 1 liter.

2.4.9.1.2 Sulfate (SO_4^{-2}) 1000 mg/L: Dissolve 1.8141 g of potassium sulfate (K_2SO_4) in reagent water and dilute to 1 liter.

2.4.9.1.3 Bromide (Br^-) 1000 mg/L: Dissolve 1.2876 g of sodium bromide (NaBr) in reagent water and dilute to 1 liter.

2.4.9.1.4 Fluoride (F^-) 1000 mg/L: Dissolve 2.1000 g of sodium fluoride (NaF) in reagent water and dilute to 1 liter.

2.4.9.1.5 Stability of standards: Stock standards are stable for at least six months when stored at 4° C.

2.4.9.2 Combined Intermediate Standard 50 mg/L Fluoride, 100 mg/L Chloride, 200 mg/L Bromide and 500 mg/L Sulfate: Pipet 5 mL of the Fluoride Stock, 10 mL of the Chloride Stock, 20 mL of the Bromide Stock and 50 mL of the Sulfate Stock into a 100 mL volumetric flask and dilute to volume with reagent water. Prepare fresh monthly.

2.4.9.3 Working Calibration Curve: Add the following volumes of the Combined Intermediate Standard (Section 2.4.9.2) to a 200 mL volumetric flask and dilute to volume. Add 1 ml of the standard eluent solution to each standard prior to diluting to volume.

Prepared Calibration Standard	Volume (mL) of Combined Intermediate Standard	Concentration (mg/L)			
		F	Br	Cl	SO_4
Blank	0.0	0.0	0.0	0.0	0.0
A	0.2	0.05*	0.2*	0.1*	0.5*
B	0.5	0.125	0.5*	0.25	1.25
C	1.0	0.25	1.0	0.5	2.50
D	2.0	0.50	2.0	1.0	5.0
E	5.0	1.25	5.0	2.5	12.5
F	10.0	2.50	10.0	5.0	25.0
G	20.0	5.0	20.0	10.0	50.0
H	25.0	6.25	25.0	12.5	62.5

* Below the reporting limit and are not used in the calibration curve.

2.4.9.4 Control Stock Solution, 1000 mg/L: Prepared as specified under Stock Standard solutions (Section 2.4.9.1).

NOTE: It is recommended that these solid reagents be obtained from a different source supplier than the solid reagents used for making the Stock Standard Solution (Section 2.4.9.1). However, if the solid reagents to be used are obtained from the same manufacturer, it must be from a different lot than the Stock Standard Solution.

3.0 SAMPLE HANDLING AND STORAGE

3.1 Sampling Procedure - There are no special considerations required due to the nature of the anions. The samples need to be chilled to 4 °C immediately following sampling.

3.2 Containers - The sampling container used is a 1 L wide mouth amber glass jar.

3.3 Storage Conditions - Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4°C.

3.4 Holding Time Limits - The holding time for soil samples is 28 days from the time of sampling to time of analysis.

3.5 Solution Verification - Calibration solutions are verified with the analysis of the daily control spikes and reference samples. Daily control spikes are prepared by a combination of individual stocks and combined intermediate stocks. The analysis of the daily control spikes serve two purposes:

3.5.1 As verification of the spiking stock solutions and,

3.5.2 For method control chart plotting.

If daily control spikes are outside of control limits due to problems with the stock, the individual stocks and control spikes must be freshly prepared and analyzed before continuing analysis of the samples.

4.0 CALIBRATION

4.1 Initial Calibration

The instrument is standardized by analyzing the calibration standards as specified in Section 2.4.9.3 and a blank. The peak heights are read off the strip chart recorder and peak area are read off the Maxima® integration system. The best fit quadratic regression equation is determined for concentration versus response.

4.2 Calibration Checks

4.2.1 Calibration Check Standard - A Calibration Check standard (a known reference standard) must be analyzed after the calibration standards. The Calibration Check standard must contain all analytes of interest and the concentration must be near the upper range of the standard curve. (The purchased calibration check standard contains all analytes, except Br^-. The calibration check standard for Br^- is prepared separately.) The acceptance criteria of the Initial Calibration Check standard is ± 15 % of the known concentration.

4.2.2 Continuing Calibration Verification Standard - A Continuing Calibration Verification Standard (CCV) must be analyzed after every ten (10) samples and at the end of analysis. The CCV is standard E. The recovery based on the standard curve must be within 10 % of the known value.

4.2.3 If the recovery of the reference standard or CCV does not meet the acceptance criteria, the standard must be rerun. If either standard still fails, the samples analyzed since the last acceptable standard must be rerun. If the samples are reanalyzed and the CCV still fails, then your Department Manager and the Laboratory Coordinator must be notified. The Laboratory Coordinator will notify USACE to determine further action.

4.3 Daily Calibration

For daily calibration, an initial calibration curve and QC checks will be performed as indicated in Sections 4.1 and 4.2.

5.0 PROCEDURE

Daily control spike samples (Section 7.2 and 7.3) and environmental samples are prepared and analyzed as follows:

5.1 Separations - The following extraction should be used for solid materials. Add 2.0 g of soil to a 50-mL, screw-cap centrifuge tube. All samples are analyzed as received and are not air dried or sieved. Add 20 mL of working eluent (Section 2.4.7) to the tubes. Prepare procedure blank by placing 20 mL of working eluent into a centrifuge tube. Shake all tubes for 30 min. Centrifuge the tubes for 15 min. Decant a 2-3 mL aliquot of the sample into a sample cup. All samples are filtered through a 0.20-um frit that is in-line in the instrument prior to analysis.

5.2 Reactions - There are no chemical reaction steps.

5.3 Instrumental Analysis - The samples are analyzed on an Ion Chromatograph as follows (See Attachment A for a typical IC run sequence):

5.3.1 Establish a stable baseline by pumping the working eluent solution through the instrument for approximately 15 to 30 minutes.

5.3.2 Pour the daily calibration standards into the sample cups in ascending order, beginning with the highest standard to calibrate the instrument, then a blank and the remainder of the standards.

5.3.3. Pour the daily control spike samples and reference sample into the sample cups and analyze.

5.3.4. Pour the environmental samples into the sample cups and analyze.

5.3.5. Reanalyze Calibration Standard E and a CCB after every ten (10) samples and at the end of the analytical run.

5.3.6. Dilute samples that have concentrations exceeding the upper standard range and reanalyze.

6.0 CALCULATION

6.1 Measure the peak height of each calibration standard and develop a quadratic regression fit for the standards by relating concentration to peak height (if using strip chart recorder) or peak area (if using the Maxima® integration system).

6.2 Verify that the correlation coefficient of the curve is ≥ 0.995.

6.3 Use the quadratic regression equation to calculate the concentration of each anion in the sample extract.

6.4 Determine the concentration of each analyte according to the following formula:

$$\text{Concentration (ug/g)} = \frac{\text{Sample Conc. (mg/L) from curve} \times \text{Extract Vol. (L)} \times \text{Dilution Factor} \times 1000}{\text{Sample Weight (g)} \times \text{\% moisture}}$$

7.0 DAILY QUALITY CONTROL

Quality control stock solutions obtained from an independent source are prepared as indicated in Section 2.4.9.4.

7.1. Intermediate Control Spike Solutions:

7.1.1 Intermediate Control Spike Solution (Low Spike): Add the following volumes of the Control Stock Standard to a 100 mL volumetric flask and dilute to volume with Type I water. Prepare the spike fresh monthly.

Analyte	Volume (mL) of Control Stock Standard	Concentration (mg/L) of Intermediate Control Spike
Fluoride	1.0	10
Chloride	2.0	20
Bromide	4.0	40
Sulfate	10.0	100

7.1.2 Intermediate Control Spike Solution (High Spike): Add the following volumes of the Control Stock Standard to a 10 mL volumetric flask and dilute to volume with Type I water.

Analyte	Volume (mL) of Control Stock Standard	Concentration (mg/L) of Intermediate Control Spike
Fluoride	1.0	100
Chloride	2.0	200
Bromide	4.0	400
Sulfate	1.0 *	1000

* For Sulfate, a 10,000 mg/L control stock is used.

7.2 The low level spike for soil samples is prepared by adding 1.0 mL of the intermediate control stock standard (low spike)(7.1.1) to 0.2 g of AEC standard soil. The spike must equilibrate with the standard soil for 1 hour before extracting the soil samples. For consistency with the MDL and upper range, the calculations of the spike recovery should use soil amount times 10 (i.e., 10.0 = 100.0 or 10.1 = 101).

Analyte	Volume (mL) of Intermediate Control Spike Standard (Low)	Low Level Spike Target (ug/g) in 2 g of AEC soil
Fluoride	1.0	5.0
Chloride	1.0	10.0
Bromide	1.0	20.0
Sulfate	1.0	50.0

7.3 The high level spike is prepared by adding 1 mL of the Control Stock Standard (high spike) (7.1.2) to 0.2 g of the AEC standard soil. The spike must equilibrate with the standard soil for 1 hour before extracting the soil samples. For consistency with the MDL and upper range, the calculations of the spike recovery should use soil amount times 10 (i.e., 0.2 = 2.0 or 0.21 = 2.1

Analyte	Volume (mL) of Intermediate Control Spike Standard (High)	High Level Spike Target (ug/g) in 2 g of AEC soil
Fluoride	1.0	50.0
Chloride	1.0	100.0
Bromide	1.0	200.0
Sulfate	1.0	500.0

7.4 One method blank (MB) must be extracted with every lot of 20 samples. The Method Blank is 0.2 g of AEC standard soil for soil samples. Follow the same procedure used for the samples.

7.5 A Continuing Calibration Blank (CCB) must be analyzed after every 10 samples. The CCB is prepared by adding 1 mL of eluent to 100 mL of Type I water.

7.6 The Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) are not required by AEC, but will be analyzed if required by the contract or project. If required, the SPM and SPMD are made by adding 1.0 mL of the Control Stock Standard to 2.0 g of sample. A SPM and SPMD will be extracted with every lot of 20 samples. The spiking concentration must be within the concentration range of the calibration standards.

7.7 Control Charts

7.7.1 Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control. Control charts are prepared for each target analyte using percent recovery data from the spiked QC samples (low and high level).

$$\%\ \text{Recovery} = \frac{\text{Found Concentration} - \text{Method Blank}}{\text{Spiked Concentration}} \times 100$$

7.7.2 To prepare control charts, the analyst will submit a data batch including spike and method blank samples to Information Services after analysis. Information Services will put the information into the USAEC control chart program. The following control charts will be returned to the analysts.

7.7.2.1 Average (x) percent recovery for the two high concentration spiked QC samples in each lot,

7.7.2.2 Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,

7.7.2.3 Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and

7.7.2.4 Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

7.7.3 The average (x), average range (R) and control limits for x and R shall be updated after each lot for the first 20 in control lots. Limits established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 in control lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

8.0 REFERENCES

8.1 Dionex Instrument Operation Manual.

8.2 U.S. Environmental Protection Agency (EPA), Test Method 300.0 (EPA-600/4-84-017).

9.0 ATTACHMENTS

9.1 Attachment A - **TYPICAL ION CHROMATOGRAPH RUN SEQUENCE**

9.2 Attachment B - **METHOD DETECTION STUDY**

9.3 Attachment C - **DEVIATIONS FROM EPA METHOD 300.0**

Attachment A - TYPICAL ION CHROMATOGRAPH RUN SEQUENCE

High standard to check instrument range	
Blank	
Standard 1 (MDL)	
Standard 2	
Standard 3	
Standard 4	
Standard 5	
Standard 6	
Standard 7	
Standard 8	
Initial calibration verification - ICV (reference)	± 15
Method blank (prep blank)	
Low Spike - SP1	
High Spike - SP2	
High Spike - SP3	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike duplicate	
Sample #2	
Sample #3	
Continuing calibration blank - CCB	
Continuing calibration verification - CCV	± 15%
Sample #4	
.	
.	
.	
Sample #13	
CCB	
CCV	± 15%
Sample #14	
.	
.	
.	
Sample #20	
CCB	
CCV	± 15%

Attachment B - METHOD DETECTION STUDY

December 16, 1993

Attachment C - DEVIATIONS FROM EPA METHOD 300.0

1. The eluent solution (Section 5.7) is a lower concentration than indicated in the method. The lower concentration of eluent is used because it provides better separation between the analytes.

Environmental Science & Engineering, Inc.
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Gainesville, Florida

DETERMINATION OF CYANIDE IN WATER BY TECHNICON (SW-846 METHOD 9012A) USAEC METHOD - CYN1 - WATER

TABLE OF CONTENTS

TITLE: **DETERMINATION OF CYANIDE IN WATER BY TECHNICON (SW-846 METHOD 9012A)**
USAEC METHOD - CYN1 - WATER

1.0 SCOPE AND APPLICATION

1.1 Analytes

1.1.1 This ESE standard operating procedure (SOP) follows SW-846 Method 9012A protocols with additional quality control requirements applicable for the Class 1 analysis under United States Army Environmental Center (USAEC) guidelines for implementation of ER1110-1-263.

1.1.2 This Standard Operating Procedure (SOP) is applicable to the quantitative determination of cyanide in water samples.

1.2 Reporting Limits, Lower and Upper Standard Range and Chemical Abstract Service (CAS) Numbers

The reporting limits, lower and upper standard range and CAS number are:

Parameter	Reporting Limits (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)	CAS Number
Cyanide (CYN)	2.5+	5.0	200	57-12-5

+ The low standard of 5.0 ug/L is equivalent to the reporting limit of 2.5 ug/L because the sample is concentrated from 500 mL to 250 mL during the distillation. The upper range of this method is 100 ug/L.

1.3 Analysis Rate

One analyst can distill approximately 90 water samples in an 8-hour day, with the current space and equipment available.

1.4 Safety Information

Acidic solutions are used in analysis. Laboratory coats and safety glasses should be worn. The acidification of solutions releases toxic cyanide gas to the air. All procedures must be completed in a hood or enclosed vessel.

1.5 Summary of Method

1.5.1 The cyanide, as hydrocyanic acid (HCN), is released by refluxing the sample with strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically. The titrimetric method is not used on samples but is used to standardize stock solutions.

1.5.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, a purple color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 570 nm for the automated method. To obtain colors of comparable intensity, the concentration of the sodium hydroxide (NaOH) must be the same in the standards, sample extract and any dilutions made to the original sample extract solution.

1.6 Method Interferences

1.6.1 Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation, should be treated by addition of bismuth nitrate, prior to distillation. Lead acetate paper may be used to check samples for the presence of sulfide.

1.6.2 Results that are biased high may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite form nitrous acid, which reacts with some organic compounds to form oximes. These compounds decompose, under test conditions, to generate HCN. Interferences due to nitrate or nitrite are eliminated by pretreatment with sulfamic acid.

1.6.3 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the samples to reduce the chlorine to chloride which does not interfere.

1.6.4 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

2.0 APPARATUS AND MATERIALS

2.1 Reflux distillation apparatus as shown in Attachment A. The boiling flask should be of one liter size with inlet tube and provision for a water cooled condenser. The distillation apparatus is sold in parts or as a complete unit in laboratory supply catalogs.

2.2 Technicon AutoAnalyzer AAII having:

2.2.1 Sampler.

2.2.2 Proportioning Pump.

2.2.3 Colorimeter equipped with a 15 mL flowcell and 570 nm filter.

2.2.4 Recorder.

2.2.5 Cyanide Manifold.

2.3 Vacuum pump.

2.4 Class A volumetric flasks - 100, 250, 500 and 1000 mL.

2.5 Class A volumetric pipets - 0.5, 1.0, 2.0, 5.0 and 10.0 mL.

2.6 Analytical balance, capable of weighing 0.01 gram.

2.7 Class A microburette - 10.0 mL.

2.8 Reagents

2.8.1 Distillation and Preparation Reagents

2.8.1.1 1.25 N Sodium Hydroxide Solution, NaOH: Dissolve 50 g of NaOH in Type I water, and dilute to one liter.

2.8.1.2 Concentrated Sulfuric Acid, H_2SO_4.

2.8.1.3 Magnesium Chloride Solution: A commercially prepared 51% Magnesium Chloride solution is purchased.

2.8.1.4 Sulfamic Acid.

2.8.2 Stock Standards and Standardization Reagents

2.8.2.1 Stock Cyanide Solution, 1000 mg CN^-/L: Dissolve 2.51g of KCN and 2 g of KOH into one liter of Type I water and dilute to one liter. Standardize against the 0.0192 N $AgNO_3$ solution. This solution may be used indefinitely, however, it must be restandardized every 6 months.

2.8.2.2 Cyanide Control Stock, 1000 mg CN^-/L: Dissolve 2.51 g of KCN and 2 g of KOH into one liter of Type I water. Standardize against the 0.0192 N $AgNO_3$ solution.

NOTE: It is recommended that this solid KCN reagent be obtained from a different supplier than the KCN used for making the Stock Cyanide Solution (Section 2.8.2.1). However, if the solid KCN reagent to be used is obtained from the same manufacturer, it must be from a different lot than the Stock Cyanide Solution.

2.8.2.3 Intermediate Cyanide Standard, 10 mg CN^-/L: Prepare fresh daily by diluting 1.0 mL of Stock Cyanide Solution (Section 2.8.2.1) to 100 mL with Type I water.

2.8.2.4 Intermediate Cyanide Control, 50 mg CN^-/L: Prepare fresh daily by diluting 5.0 mL of Cyanide Control Stock (Section 2.8.2.2) to 100 mL with Type I water.

2.8.2.5 Working Calibration Curve: Add the following volumes of the Intermediate Cyanide Standard solution (Section 2.8.2.3) to a 100 mL volumetric flask. Bring to volume using 0.25N NaOH. Prepare standards fresh daily.

Volume of Intermediate Cyanide Control (mL)	Concentration of Cyanide Calibration Standards (mg/L)
0.0	0.0
0.05	0.005
0.10	0.010
0.25	0.025
0.50	0.050
0.60	0.060
1.00	0.100
2.00	0.200

2.8.2.6 Standard Silver Nitrate Solution, 0.0192 N: A commercially prepared 0.0192 N $AgNO_3$ solution is purchased. This solution must be stored in a brown bottle, to prevent photodegradation, and must be restandardized every 6 months. Standardize against a standard NaCl solution (Section 2.8.2.10).

2.8.2.7 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine into 100 mL of acetone. This solution must be prepared fresh daily.

2.8.2.8 0.25 N Sodium Hydroxide Solution: Dissolve 10 g of NaOH in Type I water and dilute to 1 liter.

2.8.2.9 0.1 N Sodium Hydroxide Solution: Dissolve 4 g of NaOH in Type I water and dilute to 1 liter.

2.8.2.10 0.0141 N Sodium Chloride solution: Dissolve 824.0 mg NaCl (dried at 140°C) in deionized water and dilute to 1 liter. 1.00 ml of solution contains 500 ug Cl^-. This solution must be prepared fresh prior to each standardization.

2.8.2.11 Potassium Chromate Indicator Solution: Dissolve 50 g K_2CrO_4 into a small aliquot of deionized water. Add $AgNO_3$ solution until a definite red precipitate is formed. Let stand 12 hours or longer, filter and dilute to 1 liter with Type I water. This solution may be used indefinitely.

2.8.3 Semi-Automated Colorimetric Reagents

2.8.3.1 Chloramine-T Solution: Dissolve 0.40g of white, water soluble Chloramine-T in Type I water and dilute to 100 mL. Prepare fresh daily.

2.8.3.2 Phosphate Buffer, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in Type I water and dilute to 1 liter.

2.8.3.3 Pyridine-Barbituric Acid Solution: Place 15 g of barbituric acid into a beaker of 1 liter volume. Add 75 mL of pyridine and mix. Slowly, add 15 mL of concentrated HCL and mix. Dilute to approximately 800 mL with Type I water and mix until all the barbituric acid has dissolved. Transfer the solution to a 1 liter volumetric flask and bring to volume. Store in a cool, dark place. This solution expires in 6 months.

Note: This solution should be prepared at least 24 hours prior to being used. This time is needed to allow for color development of the pyridine. Otherwise, significant baseline drift can occur.

2.8.3.4 Sampler Wash: Dissolve 10 g of NaOH in Type I water and dilute to 1 liter. Add 0.5 mL Brij-35.

3.0 SAMPLE HANDLING AND STORAGE

3.1 Sampling Procedure - The samples need to be preserved with NaOH to a pH > 12 and chilled to 4 deg. Celsius (°C) immediately following sampling.

3.2 Containers - Sampling containers used for this method are 1 L plastic cubitainers.

3.3 Storage Conditions - Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4°C.

3.4 Holding Time Limits - The holding times for water samples, that are preserved, is 14 days from the time of sampling to the time of analysis.

3.5 Solution Verification - Stock standards are standardized with $AgNO_3$. Calibration solutions are verified with the analysis of daily control spikes and references. Spiking solutions are prepared monthly and are verified prior to use by comparison to the calibration standards. All standards are maintained at 4°C.

4.0 CALIBRATION

4.1 Initial Calibration

The instrument is standardized by analyzing the calibration standards specified in Section 2.8.2.5 and a blank. The absorbance is read at 570 nm and the peak heights are read off the strip chart recorder. The linear regression equation is determined for concentration versus response.

4.2 Calibration Checks

4.2.1 Calibration Check Standard - A Calibration Check standard (a known reference standard) must be analyzed after the calibration standards. The Calibration Check standard must contain all analytes of interest and the concentration must be near the upper range of the standard curve. The acceptance criteria of the Initial Calibration Check standard is ± 15 % of the known concentration.

4.2.2 Continuing Calibration Verification Standard - A Continuing Calibration Verification Standard (CCV) must be analyzed after every ten (10) samples and at the end of the analysis. The CCV is the 1.0 ug/L standard. The recovery based on the standard curve must be within 15 % of the known value.

4.2.3 If the recovery of the reference standard or CCV does not meet the acceptance criteria, the reference standard or CCV must be rerun. If either reference standard or CCV still fails, the samples analyzed since the last acceptable reference or CCV standard must be rerun. If the samples are reanalyzed and the CCV still fails, then your Department Manager and the Laboratory Coordinator must be notified. The Laboratory Coordinator will notify USACE to determine further action.

4.3 Daily Calibration

For daily calibration, an initial calibration curve and QC checks will be performed as indicated in Sections 4.1 and 4.2.

5.0 PROCEDURE

5.1 Standardization of $AgNO_3$ solution

5.1.1 Fill a 10 mL class A microburette with standard $AgNO_3$ solution (Section 2.8.2.6).

5.1.2 Titrate three blanks as follows: Pipet 10 mL of Type I water into an Erlenmeyer flask. Add 100 mL of Type I water. Adjust the pH to between 7 and 10 using NaOH or H_2SO_4, as appropriate. Add 0.5 mL of Potassium Chromate indicator (Section 2.8.2.11). Titrate with standard $AgNO_3$ titrant to a pinkish-yellow endpoint. Be consistent in endpoint recognition. Record the volume of titrant used in mL.

5.1.3 Titrate three individual 10 mL aliquots of the 0.0141 N NaCl solution in the same manner as the blanks (Section 5.1.2). Record the volume of titrant used in mL.

5.1.4 Calculate the exact normality of the $AgNO_3$ solution by the following equation:

$$\text{Normality of } AgNO_3 = \frac{(10 \text{ mL}) \times (0.0141N \text{ NaCl})}{A-B}$$

A = average mL used to titrate NaCl.

B = average mL used to titrate blank.

5.2 Standardization of Stock Standard Cyanide Solutions

5.2.1 Titrate three blanks as follows: Pipet 10 mL of Type I water into an Erlenmeyer flask. Add 100 mL of 0.1 N NaOH (Section 2.8.2.9) and 0.5 mL of the Rhodanine indicator solution (Section 2.8.2.7). Titrate with the standard $AgNO_3$ titrant to the first change in color from a canary yellow to a salmon hue. Record the volume of titrant used in mL.

5.2.2 Titrate three 10 mL aliquots of the Stock Cyanide Solution (Section 2.8.2.1) in the same manner as the blanks. Record the volume of titrant used in mL.

5.2.3 Calculate the concentration of cyanide in the Stock Cyanide Solution by using the following equation:

$$\text{mg } CN^-/L = (C-D) \times \frac{N \text{ } AgNO_3}{\text{mL } CN^- \text{ Stock}} \times \frac{2\text{eq } CN^-}{1\text{eq Ag}} \times \frac{26\text{eq}CN^-}{1\text{eq}CN^-} \times \frac{1000\text{mg}}{1\text{g}}$$

C = average mL used to titrate stock standard cyanide solution.

D = average mL used to titrate blank

N = Normality of $AgNO_3$

5.2.4 Standardize the Cyanide Control Stock solution (Section 2.8.2.2) by following the same procedure that was performed to standardize the Stock Standard Cyanide Solutions.

5.3 Distillation

5.3.1 Using a funnel, place 500 mL of sample, or an aliquot diluted to 500 mL, in a one liter boiling flask, along with several boiling chips. Add 50 mL of NaOH solution (Section 2.8.1.1) to the absorbing tube. Dilute, if necessary, with Type I water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train (see Attachment A).

5.3.2 Refer to the "**CAUTION**" indicated below before performing this step: Start a slow stream of air to enter the boiling flask by adjusting the vacuum source.

CAUTION: The bubble rate will not remain constant after the reagents have been added or while heat is being applied to the flask. It will be necessary to readjust the air rate, occasionally, to prevent the solution in the boiling flask from backing up into the air inlet tube.

5.3.3 Add approximately 2 g of sulfamic acid to the samples after the air rate has been set. Rinse the funnel with Type I water before going to Section 5.3.4.

5.3.4 Slowly, add 25 mL of concentrated sulfuric acid (Section 2.8.1.2) to the sample. Rinse the funnel with Type I water and follow this with the addition of 20 mL of magnesium chloride solution (Section 2.8.1.3) and wash down with a stream of water. Connect the air inlet tube and adjust the vacuum so that approximately 2 bubbles of air/sec enter the boiling flask through the inlet tube.

5.3.5 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour after the solution begins to boil. Turn the heat off and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect the absorber, close off the vacuum source and rinse with Type I water. Add all rinses to the absorber tube.

5.3.6 Drain the solution from the absorber into a 250 mL volumetric flask and bring to volume with Type I water washings from the absorber tube.

5.4 Chemical Reactions

Cyanide as HCN is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing NaOH solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

5.5 Instrumental Analysis - The samples are analyzed on a Technicon as follows (see Attachment C for a typical Technicon run sequence):

5.5.1 Set up the manifold as shown in Attachment B.

5.5.2 Check tubing for flatness and breaks; replace as needed.

5.5.3 Allow the colorimeter and recorder to warm up for 30 minutes.

5.5.4 Set Cam to 1:4. While running sampler wash and developing reagents set the baseline to 5 chart units.

5.5.5 Be sure to note date, type of analysis, name and standard calibration settings at the beginning of each strip chart.

5.5.6 Analyze a 0.200 mg/mL standard to determine chart recorder full scale. Set the 0.200 mg/mL standard to full scale (approximately 90 charts units) using the standard calibration knob.

5.5.7 Analyze the calibration standards in order of increasing concentration. Place a Type I water wash cup between each sample cup.

5.5.8 Analyze the daily quality control samples and reference sample.

5.5.9 Analyze the samples. Be sure to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) after every 10 samples.

5.5.10 Dilute samples that have concentrations exceeding the upper standard range and reanalyze.

5.5.11 End the run with a CCV and CCB to ensure that instruments have maintained stability throughout the run.

6.0 CALCULATION

6.1 Measure the peak height of each of the calibration standards and develop a linear regression fit for the standards by relating concentration to peak height.

6.2 Apply the linear regression equation, developed in Section 6.1, to the peak heights obtained for the samples and quality control standards to determine the concentration of cyanide.

6.3 To determine the concentration of cyanide in the original sample the following example equation should be used:

$$\text{Sample conc.} = \frac{\text{Curve conc. x Dilution Factor x Final Distillate Volume}}{\text{Sample Volume}}$$

7.0 QUALITY CONTROL

7.1 One Method blank (MB) must be digested with every lot. The Method Blank consists of 500 mL of Type I water. Follow the same procedure used for the samples.

7.2 A Continuing Calibration Blank (CCB) must be analyzed after every 10 samples. The CCB is the 0.25 N NaOH solution (Section 2.8.2.8).

7.3 Standard Spikes are prepared by adding the following volumes of the AEC Intermediate Cyanide Control solution (Section 2.8.2.4) to 500 mL of Type I water. Follow the same procedure used for the samples.

Daily Control Spike Sample Prepared	Volume (mL) of AEC Intermediate Spike Solution Spiked into 500 mL	Concentration of Control Spike Solution (ug/L)
Blank	0	0
Low	0.05	5
High	0.5	50
High	0.5	50

7.4 The Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) will be analyzed at a frequency of 5 %. Two 500 mL aliquots of a water sample are each spiked with 0.5 mL of the Intermediate Cyanide Control Spike solution (Section 2.8.2.4). A SPM and SPMD will be extracted and analyzed for every 20 samples. Spiking into the matrix must be done prior to distillation and analysis.

7.5 Control Charts

7.5.1 Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control. Control charts are prepared for each target analyte using percent recovery data from the spiked QC samples (low and high level).

$$\% \text{ Recovery} = \frac{\text{Found Concentration - Method Blank}}{\text{Spiked Concentration}} \times 100$$

7.5.2 To prepare control charts, the analyst will submit a data batch including spike and method blank samples to Information Services after analysis. Information Services will put the information into the USAEC control chart program. The following control charts will be returned to the analysts.

7.5.2.1 Average (x) percent recovery for the two high concentration spiked QC samples in each lot,

7.5.2.2 Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,

7.5.2.3 Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and

7.5.2.4 Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

7.5.3 The average (x), average range (R) and control limits for x and R shall be updated after each lot for the first 20 in control lots. Limits established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 in control lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

8.0 REFERENCES

Test Methods for Evaluating Solid Waste (EPA Method 9012A), EPA-SW-846, 3rd Edition, November 1990.

9.0 ATTACHMENTS

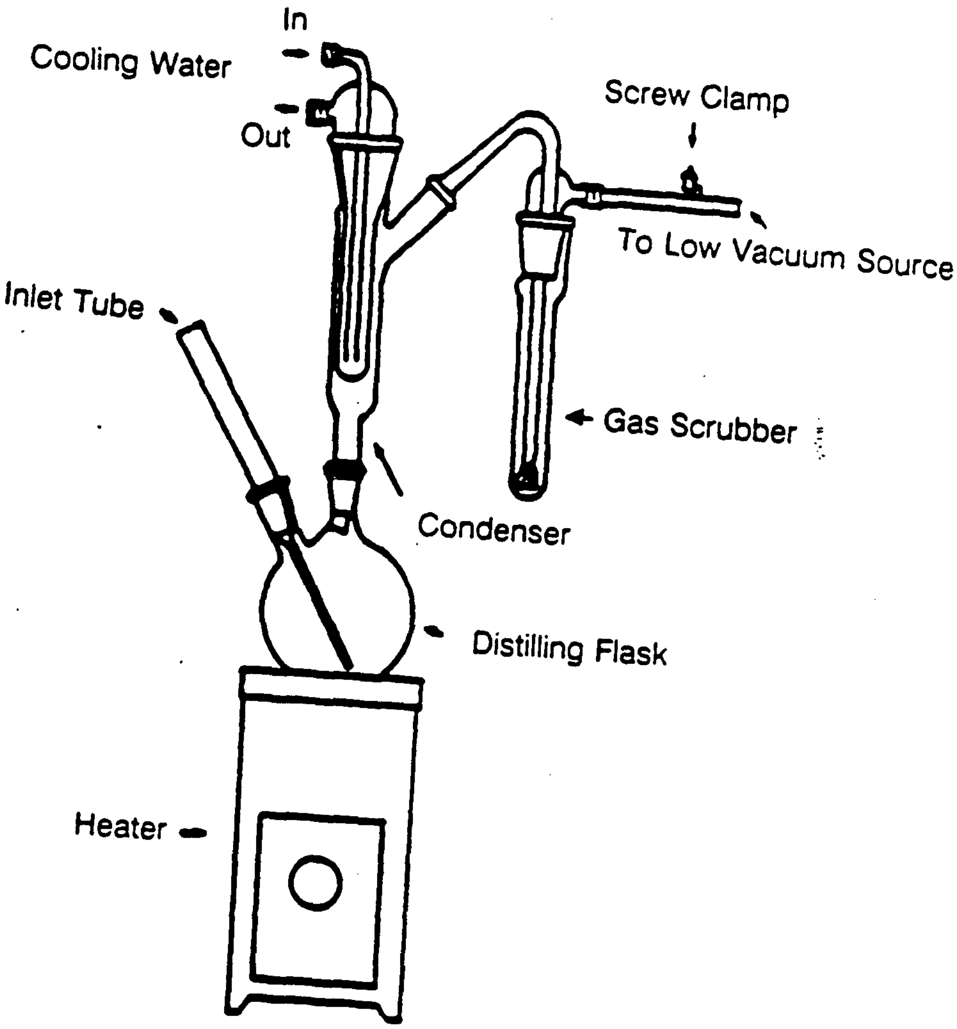
9.1 Attachment A - **DISTILLATION APPARATUS**

9.2 Attachment B - **AUTOANALYZER SCHEMATIC**

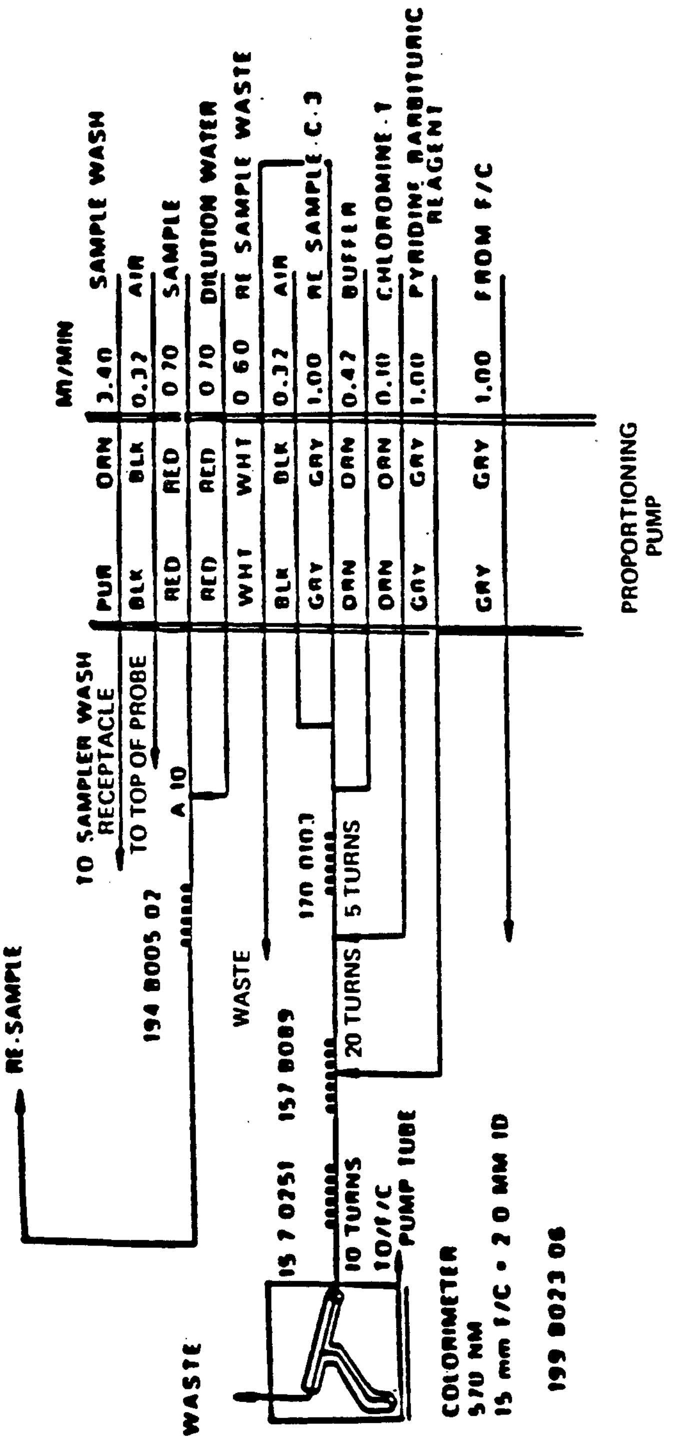
9.3 Attachment C - **TYPICAL TECHNICON RUN SEQUENCE**

9.4 Attachment D - **METHOD DETECTION STUDY**

Attachment A - DISTILLATION APPARATUS



Attachment B - AUTOANALYZER SCHEMATIC



Attachment C - TYPICAL TECHNICON RUN SEQUENCE

High standard to check instrument range	
Blank	
Standard 1 (MDL)	
Standard 2	
Standard 3	
Standard 4	
Standard 5	
Standard 6	
Standard 7	
Initial calibration blank - ICB	
Initial calibration verification - ICV (reference)	±15 %
Method blank (prep blank)	
Low Spike - SP1	
High Spike - SP2	
High Spike - SP3	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike duplicate	
Sample #2	
Sample #3	
Sample #4	
Continuing calibration blank - CCB	
Continuing calibration verification - CCV	± 15%
Sample #5	
.	
.	
.	
Sample #14	
CCB	
CCV	± 15%
Sample #15	
.	
.	
.	
Sample #24	
CCB	
CCV	± 15%

Attachment D - METHOD DETECTION STUDY

METHOD DETECTION LIMIT STUDY

Laboratory Name: Environmental Science & Engineering, Inc. (ESE)
Address: P.O. Box 1703, Gainesville, Florida, 32602-1703
Manager: Dr. John J. Mousa, Director, Gainesville Laboratory
Phone: (904) 332-3318

Method: Cyanide in Water (EPA Method 9012A)

Compound	R1 (ug/L)	R2 (ug/L)	R3 (ug/L)	R4 (ug/L)	R5 (ug/L)	R6 (ug/L)	R7 (ug/L)	X (ug/L)	S	MDL (ug/L)
Cyanide	5.150	5.150	4.890	4.890	5.150	4.890	5.410	5.076	1.965	0.62

Note: Cyanide was spiked at 4.60 ug/L

R = Actual concentration for each replicate 1-7
X = Average concentration
S = Standard deviation
ug/L = microgram per liter

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

DETERMINATION OF CYANIDE IN SOIL BY TECHNICON (MODIFIED SW-846 METHOD 9012A) USAEC METHOD - CYN1 - SOIL

TABLE OF CONTENTS

TITLE: DETERMINATION OF CYANIDE IN SOIL BY TECHNICON (MODIFIED SW-846 METHOD 9012A) USAEC METHOD - CYN1 - SOIL

1.0 SCOPE AND APPLICATION

1.1 Analytes

1.1.1 This ESE standard operating procedure (SOP) follows SW-846 9012A protocols with additional quality control requirements applicable for the Class 1 analysis under United States Army Environmental Center (USAEC) guidelines for implementation of ER1110-1-263.

1.1.2 This Standard Operating Procedure (SOP) is applicable to the quantitative determination of cyanide in soil and sediment samples.

1.2 Reporting Limits, Lower and Upper Standard Range and Chemical Abstract Service (CAS) Numbers

The reporting limits, lower and upper standard range and CAS number are:

Parameter	Reporting Limits (ug/g)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)	CAS Number
Cyanide (CYN)	0.25	5.0	200	57-12-5

1.3 Analysis Rate

One analyst can distill approximately 90 soil samples in an 8-hour day, with the current space and equipment available.

1.4 Safety Information

Acidic solutions are used in the analysis. Laboratory coats and safety glasses should be worn. The acidification of solutions releases toxic cyanide gas to the air. All procedures must be completed in a hood or enclosed vessel.

1.5 Summary of Method

1.5.1 Total cyanide of solid matrices can be determined by placing 5.0 g of sample with 500 mL of Type I water in a distillation flask and then following the normal distillation procedures. The cyanide, as hydrocyanic acid (HCN), is released by refluxing the sample with strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically. The titrimetric method is not used on samples but is used to standardize stock solutions.

1.5.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, a purple color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 570 nm for the automated method. To obtain colors of comparable intensity, the concentration of the sodium hydroxide (NaOH) must be the same in the standards, sample extract and any dilutions made to the original sample extract solution.

1.6 Method Interferences

1.6.1 Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation, should be treated by addition of bismuth nitrate, prior to distillation. Lead acetate paper may be used to check samples for the presence of sulfide.

1.6.2 Results that are biased high may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite form nitrous acid, which reacts with some organic compounds to form

oximes. These compounds decompose, under test conditions, to generate HCN. Interferences due to nitrate or nitrite are eliminated by pretreatment with sulfamic acid.

1.6.3 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the samples to reduce the chlorine to chloride which does not interfere.

1.6.4 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

2.0 APPARATUS AND MATERIALS

2.1 Reflux distillation apparatus as shown in Attachment A. The boiling flask should be of one liter size with inlet tube and provision for a water cooled condenser. The distillation apparatus is sold in parts or as a complete unit in laboratory supply catalogs.

2.2 Technicon AutoAnalyzer AAII having:

2.2.1 Sampler.

2.2.2 Proportioning Pump.

2.2.3 Colorimeter equipped with a 15 mL flowcell and 570 nm filter.

2.2.4 Recorder.

2.2.5 Cyanide Manifold.

2.3 Vacuum pump.

2.4 Class A volumetric flasks - 100, 250, 500 and 1000 mL.

2.5 Class A volumetric pipets - 0.5, 1.0, 2.0, 5.0 and 10.0 mL.

2.6 Analytical balance, capable of weighing 0.01 gram.

2.7 Class A microburette - 10.0 mL.

2.8 Reagents

2.8.1 Distillation and Preparation Reagents

2.8.1.1 1.25 N Sodium Hydroxide Solution, NaOH: Dissolve 50 g of NaOH in Type I water, and dilute to one liter.

2.8.1.2 Concentrated Sulfuric Acid, H_2SO_4.

2.8.1.3 Magnesium Chloride Solution: A commercially prepared 51% Magnesium Chloride solution is purchased.

2.8.1.4 Sulfamic Acid.

2.8.2 Stock Standards and Standardization Reagents

2.8.2.1 Stock Cyanide Solution, 1000 mg CN^-/L: Dissolve 2.51g of KCN and 2 g of KOH into one liter of Type I water and dilute to one liter. Standardize against the 0.0192 N $AgNO_3$ solution. This solution may be used indefinitely, however, it must be restandardized every 6 months.

2.8.2.2 Cyanide Control Stock, 1000 mg CN^-/L: Dissolve 2.51 g of KCN and 2 g of KOH into one liter of Type I water. Standardize against the 0.0192 N $AgNO_3$ solution.

NOTE: It is recommended that this solid KCN reagent be obtained from a different supplier than the KCN used for making the Stock Cyanide Solution (Section 2.8.2.1). However, if the solid KCN reagent to be used is obtained from the same manufacturer, it must be from a different lot than the Stock Cyanide Solution.

2.8.2.3 Intermediate Cyanide Standard, 10 mg CN^-/L: Prepare fresh daily by diluting 1.0 mL of Stock Cyanide Solution (Section 2.8.2.1) to 100 mL with Type I water.

2.8.2.4 Intermediate Cyanide Control, 50 mg CN^-/L: Prepare fresh daily by diluting 5.0 mL of Cyanide Control Stock (Section 2.8.2.2) to 100 mL with Type I water.

2.8.2.5 Working Calibration Curve: Add the following volumes of the Intermediate Cyanide Standard solution (Section 2.8.2.3) to a 100 mL volumetric flask. Bring to volume using 0.25N NaOH. Prepare standards fresh daily.

Volume of Intermediate Cyanide Control (mL)	Concentration of Cyanide Calibration Standards (mg/L)
0.0	0.0
0.05	0.005
0.10	0.010
0.25	0.025
0.50	0.050
0.60	0.060
1.00	0.100
2.00	0.200

2.8.2.6 Standard Silver Nitrate Solution, 0.0192 N: A commercially prepared 0.0192 N $AgNO_3$ solution is purchased. This solution must be stored in a brown bottle, to prevent photodegradation, and must be restandardized every 6 months. Standardize against a standard NaCl solution (Section 2.8.2.10).

2.8.2.7 Rhodanine indicator: Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine into 100 mL of acetone. This solution must be prepared fresh daily.

2.8.2.8 0.25 N Sodium Hydroxide Solution: Dissolve 10 g of NaOH in Type I water and dilute to 1 liter.

2.8.2.9 0.1 N Sodium Hydroxide Solution: Dissolve 4 g of NaOH in Type I water and dilute to 1 liter.

2.8.2.10 0.0141 N Sodium Chloride solution: Dissolve 824.0 mg NaCl (dried at 140°C) in deionized water and dilute to 1 liter. 1.00 ml of solution contains 500 ug Cl^-. This solution must be prepared fresh prior to each standardization.

2.8.2.11 Potassium Chromate Indicator Solution: Dissolve 50 g K_2CrO_4 into a small aliquot of deionized water. Add $AgNO_3$ solution until a definite red precipitate is formed. Let stand 12 hours or longer, filter and dilute to 1 liter with Type I water. This solution may be used indefinitely.

2.8.3 Semi-Automated Colorimetric Reagents

2.8.3.1 Chloramine-T Solution: Dissolve 0.40g of white, water soluble Chloramine-T in Type I water and dilute to 100 mL. Prepare fresh daily.

2.8.3.2 Phosphate Buffer, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in Type I water and dilute to 1 liter.

2.8.3.3 Pyridine-Barbituric Acid Solution: Place 15 g of barbituric acid into a 1 liter beaker. Add 75 mL of pyridine and mix. Slowly, add 15 mL of concentrated HCL and mix. Dilute to approximately 800 mL with Type I water and mix until all the barbituric acid has dissolved. Transfer the solution to a 1 liter volumetric flask and bring to volume. Store in a cool, dark place. This solution expires in 6 months.

Note: This solution should be prepared at least 24 hours prior to being used. This time is needed to allow for color development of the pyridine. Otherwise, significant baseline drift can occur.

2.8.3.4 Sampler Wash: Dissolve 10 g of NaOH in Type I water and dilute to 1 liter. Add 0.5 mL Brij-35.

3.0 SAMPLE HANDLING AND STORAGE

3.1 Sampling Procedure - Samples for total cyanide analysis shall be placed in cleaned, wide-mouthed, glass jar with a Teflon lined lid. Sample jars shall be placed in a temperature-controlled [4°C] chest immediately following sampling and delivered to the laboratory as soon as possible.

3.2 Containers - Sampling containers used for this method are 1 L, wide-mouthed, glass bottle.

3.3 Storage Conditions - Samples are to be kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4°C.

3.4 Holding Time Limits - The holding times for soil samples is 14 days from the time of sampling to the time of analysis.

3.5 Solution Verification - Stock standards are standardized with $AgNO_3$. Calibration solutions are verified with the analysis of daily control spikes and references. Spiking solutions are prepared monthly and are verified prior to use by comparison to the calibration standards. All standards are maintained at 4°C.

4.0 CALIBRATION

4.1 Initial Calibration

The instrument is standardized by analyzing the calibration standards specified in Section 2.8.2.5 and a blank. The absorbance is read at 570 nm and the

peak heights are read off the strip chart recorder. The linear regression equation is determined for concentration versus response.

4.2 Calibration Checks

4.2.1 Calibration Check Standard - A Calibration Check standard (a known reference standard) must be analyzed after the calibration standards. The acceptance criteria of the Initial Calibration Check standard is $\pm$ 15 % of the true value.

4.2.2 Continuing Calibration Verification Standard - A Continuing Calibration Verification Standard (CCV) must be analyzed after every ten (10) samples and at the end of the analysis. The CCV is the 1.0 ug/L standard. The recovery based on the standard curve must be within 15 % of the true value.

4.2.3 If the recovery of the reference standard or CCV does not meet the acceptance criteria the reference standard or CCV must be rerun. If either the reference standard or CCV still fails, the samples analyzed since the last acceptable reference standard or CCV must be rerun. If the samples are reanalyzed and the CCV still fails, then your Department Manager and the Laboratory Coordinator must be notified. The Laboratory Coordinator will notify USACE to determine further action.

4.3 Daily Calibration

For daily calibration, an initial calibration curve and QC checks will be performed as indicated in Sections 4.1 and 4.2.

5.0 PROCEDURE

5.1 Standardization of $AgNO_3$ solution

5.1.1 Fill a 10 mL class A microburette with standard $AgNO_3$ solution (Section 2.8.2.6).

5.1.2 Titrate three blanks as follows: Pipet 10 mL of Type I water into an Erlenmeyer flask. Add 100 mL of Type I water. Adjust the pH to between 7 and 10 using NaOH or H_2SO_4, as appropriate. Add 0.5 mL of Potassium Chromate indicator (Section 2.8.2.11). Titrate with standard $AgNO_3$ titrant to a pinkish-yellow endpoint. Be consistent in endpoint recognition. Record the volume of titrant used in mL.

5.1.3 Titrate three individual 10 mL aliquots of the 0.0141 N NaCl solution in the same manner as the blanks (Section 5.1.2). Record the volume of titrant used in mL.

5.1.4 Calculate the exact normality of the $AgNO_3$ solution by the following equation:

$$\text{Normality of } AgNO_3 = \frac{(10\text{ mL}) \times (0.0141\text{N NaCl})}{A\text{-}B}$$

A = average mL used to titrate NaCl.

B = average mL used to titrate blank.

5.2 Standardization of Stock Standard Cyanide Solutions

5.2.1 Titrate three blanks as follows: Pipet 10 mL of Type I water into an Erlenmeyer flask. Add 100 mL of 0.1 N NaOH (Section 2.8.2.9) and 0.5 mL of the Rhodanine indicator solution (Section 2.8.2.7). Titrate with the standard $AgNO_3$ titrant to the first change in color from a canary yellow to a salmon hue. Record the volume of titrant used in mL.

5.2.2 Titrate three 10 mL aliquots of the Stock Cyanide Solution (Section 2.8.2.1) in the same manner as the blanks. Record the volume of titrant used in mL.

5.2.3 Calculate the concentration of cyanide in the Stock Cyanide Solution by using the following equation:

$$\text{mg CN}^-/\text{L} = (\text{C-D}) \times \frac{\text{N AgNO}_3}{\text{mL CN}^- \text{ Stock}} \times \frac{\text{2eq CN}^-}{\text{1eq Ag}} \times \frac{\text{26eqCN}^-}{\text{1eqCN}^-} \times \frac{\text{1000mg}}{\text{1g}}$$

C = average mL used to titrate stock standard cyanide solution.

D = average mL used to titrate blank

N = Normality of $AgNO_3$

5.2.4 Standardize the Cyanide Control Stock solution (Section 2.8.2.2) by following the same procedure that was performed to standardize the Stock Standard Cyanide Solutions.

5.3 Distillation

5.3.1 Place 5.0 g of soil sample in a one liter boiling flask and add several boiling chips and 500 mL of Type I water. Add 50 mL of NaOH solution (Section 2.8.1.1) to the absorbing tube. Dilute, if necessary, with Type I water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train (see Attachment A).

5.3.2 Refer to the "**CAUTION**" indicated below before performing this step: Start a slow stream of air to enter the boiling flask by adjusting the vacuum source.

CAUTION: The bubble rate will not remain constant after the reagents have been added or while heat is being applied to the flask. It will be necessary to readjust the air rate, occasionally, to prevent the solution in the boiling flask from backing up into the air inlet tube.

5.3.3 Add approximately 2 g of sulfamic acid to the samples after the air rate has been set. Rinse the funnel with Type I water before going to Section 5.3.4.

5.3.4 Slowly, add 25 mL of concentrated sulfuric acid (Section 2.8.1.2) to the sample. Rinse the funnel with Type I water and follow this with the addition of 20 mL of magnesium chloride solution (Section 2.8.1.3) and wash down with a stream of water. Connect the air inlet

tube and adjust the vacuum so that approximately 2 bubbles of air/sec enter the boiling flask through the inlet tube.

5.3.5 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour after the solution begins to boil. Turn the heat off and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect the absorber, close off the vacuum source and rinse with Type I water. Add all rinses to the absorber tube.

5.3.6 Drain the solution from the absorber into a 250 mL volumetric flask and bring to volume with Type I water washings from the absorber tube. Be sure to include any absorber solution that has been pushed over into the traps.

5.4 Chemical Reactions

Cyanide as HCN is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing NaOH solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

5.5 Instrumental Analysis - The samples are analyzed on a Technicon as follows (see Attachment C for a typical Technicon run sequence):

5.5.1 Set up the manifold as shown in Attachment B.

5.5.2 Check tubing for flatness and breaks; replace as needed.

5.5.3 Allow the colorimeter and recorder to warm up for 30 minutes.

5.5.4 Set Cam to 1:4. While running sampler wash and developing reagents set the baseline to 5 chart units.

5.5.5 Be sure to note date, type of analysis, name and standard calibration settings at the beginning of each strip chart.

5.5.6 Analyze a 0.200 mg/mL standard to determine chart recorder full scale. Set the 0.200 mg/mL standard to full scale (approximately 90 charts units) using the standard calibration knob.

5.5.7 Analyze the calibration standards in order of increasing concentration. Place a Type I water wash cup between each sample cup.

5.5.8 Analyze the daily quality control samples and reference sample.

5.5.9 Analyze the samples. Be sure to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) after every 10 samples.

5.5.10 Dilute samples that have concentrations exceeding the upper standard range and reanalyze.

5.5.11 End the run with a CCV and CCB to ensure that instruments have maintained stability throughout the run.

6.0 CALCULATION

6.1 Measure the peak height of each of the calibration standards and develop a linear regression fit for the standards by relating concentration to peak height.

6.2 Use the linear regression equation, developed in 6.1, to the peak heights obtained for the samples and quality control standards to determine the concentration of cyanide.

6.3 To determine the concentration of cyanide in the original sample the following example equation should be used:

$$\text{Sample conc.} = \frac{\text{Curve conc. x Dilution Factor x Final Distillation Volume}}{\text{Sample Weight x \% moisture}}$$

7.0 QUALITY CONTROL

7.1 One Method blank (MB) must be digested with every lot. The Method Blank consists of 5.0 g of AEC standard soil and 500 mL of Type I water. Follow the same procedure used for the samples.

7.2 A Continuing Calibration Blank (CCB) must be analyzed after every 10 samples. The CCB is the 0.25 N NaOH solution (Section 2.8.2.8).

7.3 Standard Spikes are prepared by adding the following volumes of the AEC Intermediate Cyanide Control solution (Section 2.8.2.4) to 5.0 g of AEC Standard soil. Follow the same procedure used for the samples.

Daily Control Spike Sample Prepared	Volume (mL) of AEC Intermediate Spike Solution	Concentration of Control Spike Solution (ug/g)
Blank	0	0
Low	0.05	0.5
High	0.5	5.0
High	0.5	5.0

7.4 The Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) will be analyzed at a frequency of 5 %. Two 5.0 g aliquots of a soil sample are each spiked with 0.5 mL of the Intermediate Cyanide Control Spike solution (Section 2.8.2.4). A SPM and SPMD will be extracted and analyzed every 20 samples. Spiking into the matrix must be done prior to distillation and analysis.

7.5 Control Charts

7.5.1 Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control. Control charts are prepared for each target analyte using percent recovery data from the spiked QC samples (low and high level).

$$\% \text{ Recovery} = \frac{\text{Found Concentration - Method Blank}}{\text{Spiked Concentration}} \times 100$$

7.5.2 To prepare control charts, the analyst will submit a data batch including spike and method blank samples to Information Services after analysis. Information Services will put the information into the USAEC control chart program. The following control charts will be returned to the analysts.

7.5.2.1 Average (x) percent recovery for the two high concentration spiked QC samples in each lot,

7.5.2.2 Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,

7.5.2.3 Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and

7.5.2.4 Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

7.5.3 The average (x), average range (R) and control limits for x and R shall be updated after each lot for the first 20 in control lots. Limits established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 in control lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

8.0 REFERENCES

Test Methods for Evaluating Solid Waste (EPA Method 9012A), EPA-SW-846, 3rd Edition, November 1990.

9.0 ATTACHMENTS

9.1 Attachment A - **DISTILLATION APPARATUS**

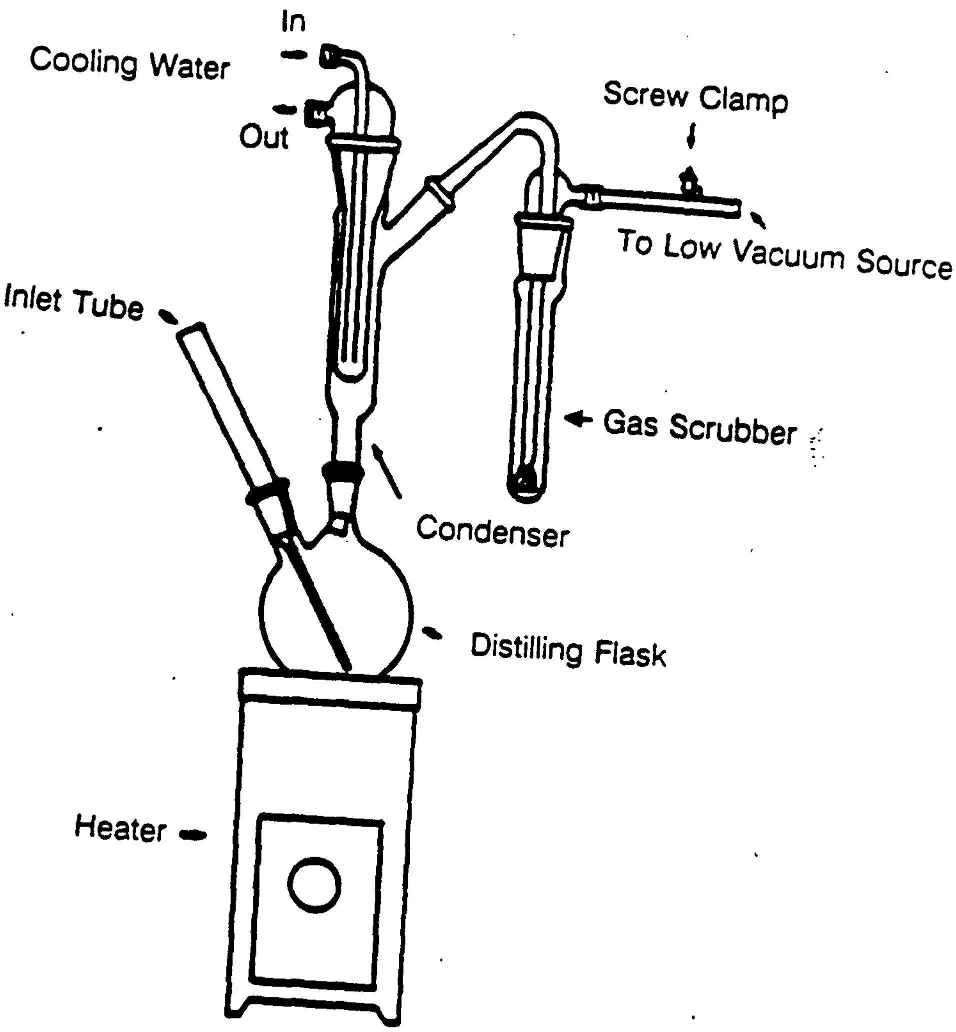
9.2 Attachment B - **AUTOANALYZER SCHEMATIC**

9.3 Attachment C - **TYPICAL TECHNICON RUN SEQUENCE**

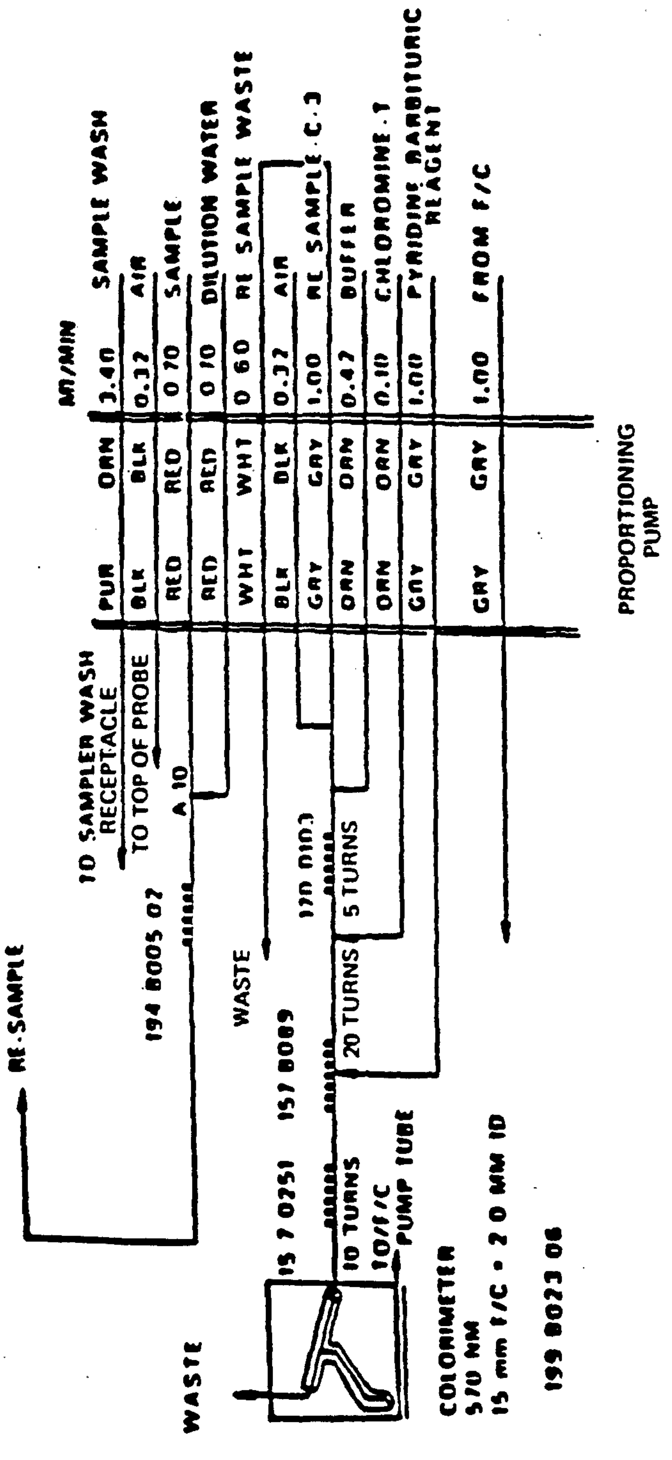
9.4 Attachment D - **METHOD DETECTION STUDY**

9.5 Attachment E - **DEVIATIONS FROM METHOD 9012A**

Attachment A - DISTILLATION APPARATUS



Attachment B - AUTOANALYZER SCHEMATIC



Attachment C - TYPICAL TECHNICON RUN SEQUENCE

High standard to check instrument range	
Blank	
Standard 1 (MDL)	
Standard 2	
Standard 3	
Standard 4	
Standard 5	
Standard 6	
Standard 7	
Initial calibration blank - ICB	
Initial calibration verification - ICV (reference)	±15
Method blank (prep blank)	
Low Spike - SP1	
High Spike - SP2	
High Spike - SP3	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike duplicate	
Sample #2	
Sample #3	
Sample #4	
Continuing calibration blank - CCB	
Continuing calibration verification - CCV	± 15%
Sample #5	
.	
.	
.	
Sample #14	
CCB	
CCV	± 15%
Sample #15	
.	
.	
.	
Sample #24	
CCB	
CCV	± 15%
.	

Attachment D - METHOD DETECTION STUDY

METHOD DETECTION LIMIT STUDY

Laboratory Name: Environmental Science and Engineering, Inc. (ESE)
Address: P.O. Box 1703, Gainesville, Florida, 32602-1703
Manager: Dr. John J. Mousa, Director, Gainesville Laboratory
Phone: (904)332-3318

Method: Cyanide in Soil (Modified EPA Method 9012A)

Compound Name	R1 (ug/g)	R2 (ug/g)	R3 (ug/g)	R4 (ug/g)	R5 (ug/g)	R6 (ug/g)	R7 (ug/g)	X (ug/g)	S	MDL (ug/g)
Cyanide	0.470	0.470	0.470	0.459	0.459	0.459	0.470	0.465	0.0059	0.018

Target concentration is 0.5 ug/g

EPA = Environmental Protection Agency
R = Actual concentration for each replicate 1-7
X = Average concentration
S = Standard deviation

October 28, 1993

Attachment E - DEVIATIONS FROM METHOD 9012A

1. Soil and sediment matrices are not included in the scope of SW-846 Method 9012A. Therefore, SW-846 Method 9012A has been modified for inclusion of soil and sediment samples in the method. Appropriate method detection limit studies support the applicability of this method to soil and sediment matrices. The modifications made are only on the distillation procedure which are as follows:

    Five grams of a soil sample are used in place of the 500 mL aliquot specified for water samples.

    A 500 mL volume of Type I water is added to the soil sample.

    The distillation procedure defined in the EPA method is then followed as written with no further deviations.

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

DETERMINATION OF TOTAL RECOVERABLE PHENOLICS IN WATER BY TECHNICON (MODIFIED SW-846 METHOD 9066A) USAEC METHOD - TPT1 - WATER

TABLE OF CONTENTS

TITLE: DETERMINATION OF TOTAL RECOVERABLE PHENOLICS IN WATER BY TECHNICON (MODIFIED SW-846 METHOD 9066A) USAEC METHOD - TPT1 - WATER

1.0 SCOPE AND APPLICATION

1.1 Analyte

1.1.1 This ESE Standard Operating Procedure (SOP) follows SW-846 Method 9066A protocols with additional quality control requirements applicable for the Class 1 analysis under United States Army Environmental Center (USAEC) guidelines for implementation of ER1110-1-263.

1.1.2 This SOP is applicable to the quantitative determination of phenol in water samples. It is not possible to differentiate between different kinds of phenols with this method.

1.2 Reporting Limit, Lower and Upper Standard Range and Chemical Abstract Service (CAS) Number

The reporting limit, lower and upper standard range and CAS number are:

Parameter	Reporting Limit (ug/L)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)	CAS Number
Phenol	2.0	2.0	100	108-95-2

1.4 Analysis Rate

One analysis can distill and analyze 32 samples, including quality control samples, in an 8 hour day.

1.5 Safety Information

Extreme care should be employed in the handling of samples and standards due to the toxicity of phenol. Process the samples in a laboratory hood using proper skin protection (i.e., gloves).

1.6 Summary of Method

This automated method is based on the distillation of phenol and subsequent reactions of the distillate with alkaline ferricyanide and 4-aminoantipyrine to form a red complex which is measured at 505 nm.

1.7 Method Interferences

1.7.1 Background contamination from plastic tubing and samples containers is eliminated by filling the wash receptacle by siphon and using glass tubes for the samples and standards.

1.7.2 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4 with H_2SO_4 and aerating briefly by stirring.

1.7.3 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate. If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

2.0 APPARATUS AND MATERIALS

2.1 Distillation apparatus, all glass, consisting of a 1 liter Pyrex distilling apparatus with Graham condenser.

2.2 Technicon AutoAnalyzer AAII, having:

2.2.1 Sampler.

2.2.2 Proportioning Pump.

2.2.3 Colorimeter equipped with a 50 mL flowcell and 505 nm filter.

2.2.4 Recorder.

2.2.5 Manifold.

2.3 Class A volumetric flasks - 100 mL.

2.4 500 mL graduated cylinders.

2.5 Class A pipets - 0.5, 1.0, 5.0 and 10.0 mL sizes.

2.6 Calibrated syringe - 1 mL.

2.7 Top loading balance.

2.8 500 mL Erlenmeyer flasks.

2.9 pH meter.

2.10 One liter flasks.

2.11 Glass sample vials.

2.12 Reagents

2.12.1 Buffered potassium ferricyanide: Dissolve 1.0 g of potassium ferricyanide, 1.55 g of boric acid and 1.875 g of potassium chloride in 400 mL of distilled water. Adjust pH to 10.3 with 1 N sodium hydroxide (Section 2.12.2) and dilute to 500 mL. Add 0.5 mL of Brij-35. Prepare fresh weekly.

2.12.2 Sodium hydroxide (NaOH), 1 N: Dissolve 40 g of NaOH in 500 mL of distilled water, cool and dilute to 1 liter.

2.12.3 4-Aminoantipyrine: Dissolve 0.325 g of 4-aminoantipyrine in 400 mL of distilled water and dilute to 500 mL. Prepare fresh daily.

2.12.4 Sulfuric Acid, H_2SO_4, concentrated.

2.12.5 Phenol Stock Standard solution, 1000 mg/L: Dissolve 1.00 g of phenol into 1 liter of distilled water. Add 0.5 mL of concentrated sulfuric acid as a preservative.

2.12.6 Phenol Control Standard solution, 1000 mg/L: Dissolve 1.00 g of phenol into 1 liter of distilled water. Add 0.5 mL of concentrated sulfuric acid as a preservative.

NOTE: It is recommended that this solid phenol reagent be obtained from a different source supplier than the phenol used for making the Stock Phenol Solution (Section 2.12.5). However, if the solid phenol reagent to be used is obtained from the same manufacturer, it must be from a different lot than the Stock Phenol Solution.

2.12.7 Intermediate Phenol Standard solution, 10 mg/L: Dilute 10 mL of the Phenol Stock Standard (Section 2.12.5) into 1 liter.

2.12.8 Intermediate Phenol Control solution, 10 mg/L: Dilute 10 mL of the Phenol Control Standard (Section 2.12.6) into 1 liter.

2.12.9 Calibration Standards: Prepare a series of standards by pipeting the following volumes of the Intermediate Phenol Standard solution (Section 2.12.7) into a series of 100 mL volumetric flasks. Prepared fresh daily.

Volume of Intermediate Phenol Standard (mL)	Concentration of Phenol Standard (ug/L)
0.0	0.0
0.02	2.0
0.05	5.0
0.10	10.0
0.25	25.0
0.50	50.0
1.00	100.0

3.0 SAMPLE HANDLING AND STORAGE

3.1 Sampling Procedure - The sample container must be rinsed two or three times with the sample being collected. The container is filled with the water sample and preserved with sulfuric acid to a pH of 2. A teflon lined screw cap is used to secure the sample.

3.2 Container - The sampling container used is a 1 L glass container with a teflon lined cap.

3.3 Storage Conditions - Samples are preserved with sulfuric acid to a pH of 2, and kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4°C.

3.4 Holding Time Limits - The holding time for water samples is 28 days from the time of sampling to time of analysis.

3.5 Solution Verification - Calibration solutions are verified with the analysis of the daily control spikes and references. Spiking solutions are prepared monthly and are verified prior to used by comparison to the calibration standards. All standard spike solutions are maintained at 4°C.

4.0 CALIBRATION

4.1 Initial Calibration

The instrument is standardized by analyzing the calibration standards specified in Section 2.12.9 and a blank. The absorbance is read at 505 nm and the peak heights are read off the strip chart recorder. The linear regression equation is determined for concentration versus response.

4.2 Calibration Checks

4.2.1 Calibration Check Standard/Initial Calibration Verification (ICV) - An ICV must be analyzed after the calibration standards. The ICV is prepared from a different source than the Stock or Control Standards, if available, or from the same source as the Control standard but prepared on a different day and/or by a different analyst from the Control stock. The concentration of the ICV is 50 ug/L. The acceptance criteria of the ICV is $\pm$ 15 % of the known concentration.

4.2.2 Continuing Calibration Verification Standard - A Continuing Calibration Verification Standard (CCV) must be analyzed after every ten (10) samples and at the end of analysis. The CCV is the 50 ug/L standard. The recovery based on the standard curve must be within 15 % of the known value.

4.2.3 If the recovery of the reference standard or CCV does not meet the acceptance criteria the standard must be rerun. If either standard still fails, the samples analyzed since the last acceptable reference standard or CCV must be rerun. If the samples are reanalyzed and the CCV still fails, then your Department Manager and the Laboratory Coordinator must be notified. The Laboratory Coordinator will notify USACE to determine further action.

4.3 Daily Calibration

For daily calibration, an initial calibration curve and QC checks will be performed as indicated in Section 4.1 and 4.2.

5.0 PROCEDURE

Daily control spike samples (Section 7.3) and environmental samples are prepared and analyzed as follows:

5.1 Distillation

5.1.1 Measure 500 mL of sample into the distillation apparatus and check that the pH is less than 4. If pH is greater than 4, adjust the pH with H_2SO_4.

5.1.2 Distill 450 mL of sample, stop the distillation, and when boiling ceases add 50 mL of warm distilled water to the flask and resume distillation until 500 mL have been collected.

5.2 Chemical Reactions - Phenolic compounds react with 4-aminoantipyrine (4AAP) in the presence of potassium ferricyanide at a pH of 10 to form a stable red complex which is measured at 505 nm.

5.3 Instrument Analysis

5.3.1 Set up the manifold as shown in Attachment A.

5.3.2 Fill the wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 liter/hr).

5.3.3 Set Cam to 20 1/2. Allow the colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Use polyethylene tubing for sample line. When new tubing is used, about 2 hours may be required to obtain a stable baseline. This two hour period may be necessary to remove the residual phenol from the tubing.

5.3.4 Analyze the calibration standards in order of increasing concentration.

5.3.5 Analyze the daily quality control samples and reference sample.

5.3.6 Analyze the samples. Be sure to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) after every 10 samples.

5.3.7 Dilute samples that have concentrations exceeding the upper standard range and reanalyze.

5.3.8 End the run with a CCV and CCB to ensure that instruments have maintained stability throughout the run.

6.0 CALCULATION

6.1 Measure the peak height of each of the calibration standards and record the peak height on the chromatogram and in the run log. Develop a linear regression fit for the standards by relating concentration to peak height. Verify that the correlation curve of the curve $\geq$ 0.995.

6.2 Measure the peak height of each sample and quality control standard. Apply the linear regression equation, developed in Section 6.1, to the peak heights obtained to determine the concentration of phenol.

6.3 The sample concentration from the curve is the final sample concentration because the final distillate volume is the same as the initial sample volume. Final sample results are corrected for sample dilutions.

7.0 QUALITY CONTROL

7.1 A Method blank (MB) must be analyzed with every lot. The MB consists of Type I water. Follow the same procedure as the samples.

7.2 A Continuing Calibration Blank (CCB) must be analyzed after every 10 samples. The CCB is Type I water.

7.3 The following daily control spike samples are prepared by adding the following volumes of the intermediate control stock (Section 2.12.8) to 500 mL of Type I water. Follow the same procedure as the samples.

Daily Control Spike Sample Prepared	Volume (mL) of AEC Intermediate Spike Solution Spiked into 500 mL	Concentration of Control Spike Solution (ug/L)
Blank	0	0
Low	0.2	4.0
High	2.0	40.0
High	2.0	40.0

7.4 The Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) are not required for AEC projects, but will be analyzed if required by the contract or project. The SPM and SPMD (50 μg/L) are made by pipeting 2.5 mL of the 10 mg/L Intermediate Phenol Control solution (Section 2.12.8) into a 500 mL volumetric flask and diluting to volume with sample. Spiking into the matrix must be done prior to distillation and analysis. The spiking concentration must be within the concentration range of the calibration standards.

7.5 Control Charts

7.5.1 Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control. Control charts are prepared for each target analyte using percent recovery data from the spiked QC samples (low and high level).

$$\% \text{ Recovery} = \frac{\text{Found Concentration - Method Blank}}{\text{Spiked Concentration}} \times 100$$

7.5.2 To prepare control charts, the analyst will submit a data batch including spike and method blank samples to Information Services after analysis. Information Services will put the information into the USAEC control chart program. The following control charts will be returned to the analysts.

Attachment D - DEVIATION FROM METHOD 9066A

1. SW-846 Method 9066A uses an automated continuous-flow analytical instrument with attached distillation apparatus and heating bath with distillation coil. ESE's Technicon TRAACS is not equipped with an attached distillation apparatus and heating bath with distillation coil. Hence, sample distillation is performed separately from analysis using an all glass distillation apparatus consisting of a 1 liter Pyrex distilling apparatus with Graham condenser.

2. Calibration standards are prepared daily and used only on the day standards are prepared. Therefore, the calibration standards are not preserved with 2 drops of concentrated sulfuric acid as required by SW-846 Method 9066A.

Attachment C - METHOD DETECTION STUDY

METHOD DETECTION LIMIT STUDY

Laboratory Name: Environmental Science & Engineering, Inc. (ESE)
Address: P.O. Box 1703, Gainesville, Florida, 32602-1703
Manager: Dr. John J. Mousa, Director, Gainesville Laboratory
Phone: (904) 332-3318

Method: Phenols in Water (EPA Method 420.2)

Compound Name	R1 (ug/L)	R2 (ug/L)	R3 (ug/L)	R4 (ug/L)	R5 (ug/L)	R6 (ug/L)	R7 (ug/L)	X (ug/L)	S	MDL (ug/L)
Phenols	9.62	9.18	9.41	9.22	9.35	8.25	8.45	9.07	0.47	- 1.58

Note: Target concentration for Phenols in water is 10 ug/L

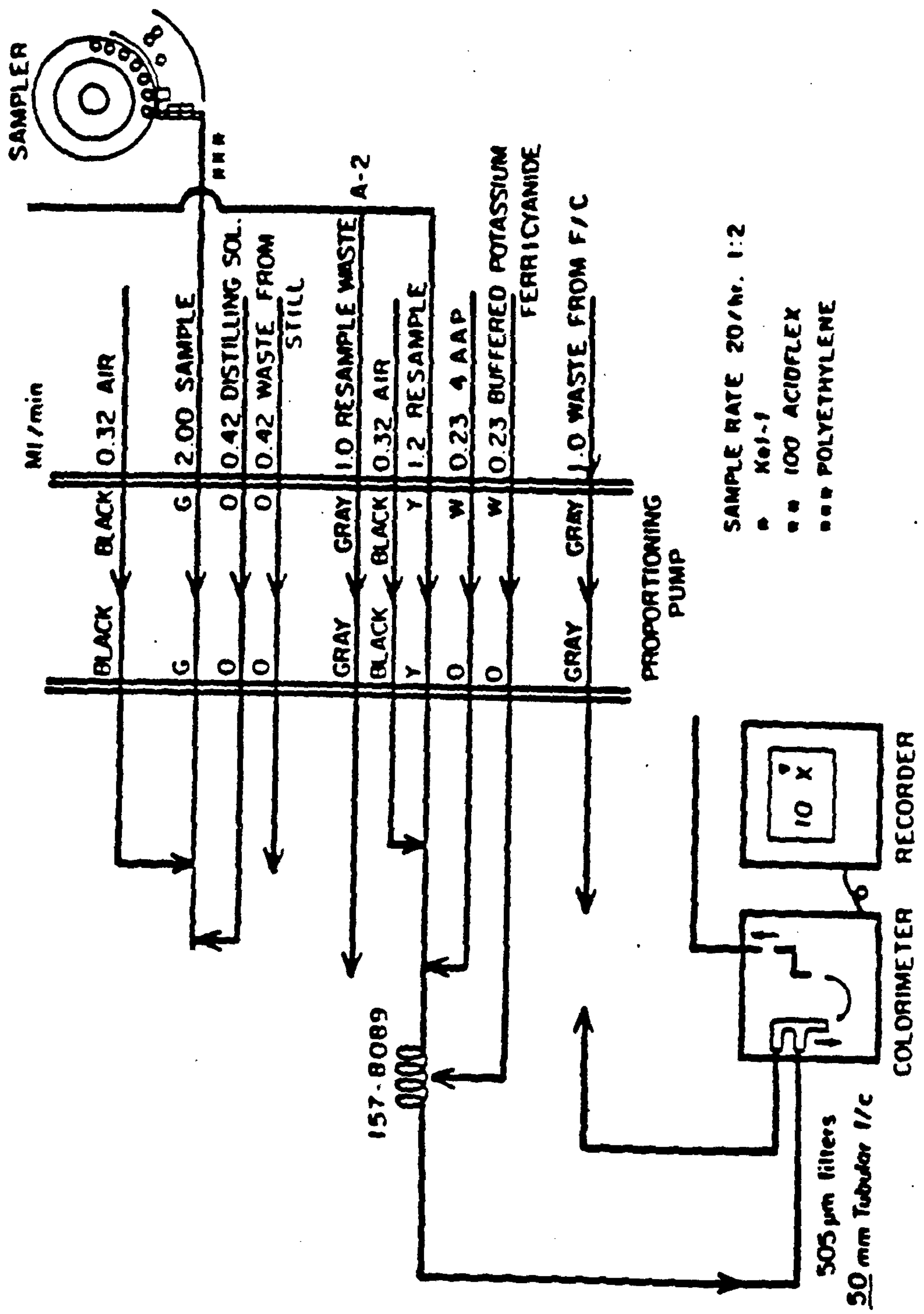
R = Actual concentration for each replicate 1-7
X = Average concentration
S = Standard deviation
ug/L = microgram per liter

October 27, 1993

Attachment B - **TYPICAL TECHNICON RUN SEQUENCE**

High standard to check instrument range	
Blank	
Standard 1 (MDL)	
Standard 2	
Standard 3	
Standard 4	
Standard 5	
Standard 6	
Initial calibration blank - ICB	
Initial calibration verification - ICV (reference)	±15 %
Method blank (prep blank)	
Low Spike - SP1	
High Spike - SP2	
High Spike - SP3	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike duplicate	
Sample #2	
Sample #3	
Sample #4	
Continuing calibration blank - CCB	
Continuing calibration verification - CCV	± 15%
Sample #5	
.	
.	
.	
Sample #14	
CCB	
CCV	± 15%
Sample #15	
.	
.	
.	
Sample #24	
CCB	
CCV	± 15%
.	

Attachment A - AUTOANALYZER SCHEMATIC



October 27, 1993

7.5.2.1 Average (x) percent recovery for the two high concentration spiked QC samples in each lot,

7.5.2.2 Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,

7.5.2.3 Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and

7.5.2.4 Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

7.5.3 The average (x), average range (R) and control limits for x and R shall be updated after each lot for the first 20 in control lots. Limits established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 in control lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

8.0 REFERENCE

8.1 Test Methods for Evaluating Solid Waste, (EPA Method 9066A) EPA-SW-846, 3rd Edition, September 1986.

8.2 Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

9.0 ATTACHMENTS

9.1 Attachment A - **AUTOANALYZER SCHEMATIC**

9.2 Attachment B - **TYPICAL TECHNICON RUN SEQUENCE**

9.3 Attachment C - **METHOD DETECTION LIMIT STUDY**

9.4 Attachment D - **DEVIATION FROM METHOD 9066**

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

DETERMINATION OF TOTAL RECOVERABLE PHENOLICS IN SOIL BY TECHNICON (MODIFIED SW-846 METHOD 9066A)
USAEC METHOD - TPT1 - SOIL

TABLE OF CONTENTS

**TITLE: DETERMINATION OF TOTAL RECOVERABLE PHENOLICS IN SOIL BY TECHNICON (MODIFIED SW-846 METHOD 9066A)
USAEC METHOD - TPT1 - SOIL**

1.0 SCOPE AND APPLICATION

1.1 Analyte

1.1.1 This ESE Standard Operating Procedure (SOP) follows SW-846 Method 9066A protocols with additional quality control requirements applicable for the Class 1 analysis under United States Army Environmental Center (USAEC) guidelines for implementation of ER1110-1-263.

1.1.2 This SOP is applicable to the quantitative determination of phenol in soil samples. It is not possible to differentiate between different kinds of phenols with this method.

1.2 Reporting Limit, Lower and Upper Standard Range and Chemical Abstract Service (CAS) Number

The reporting limit, lower and upper standard range and CAS number are:

Parameter	Reporting Limit (ug/g)	Lower Standard Range (ug/L)	Upper Standard Range (ug/L)	CAS Number
Phenol	1.0	2.0	100	108-95-2

1.4 Analysis Rate

One analyst can distill 32 samples, including quality control samples, in an 8 hour day.

1.5 Safety Information

Extreme care should be employed in the handling of samples and standards due to the toxicity of phenol. Process the samples in a laboratory hood using proper skin protection (i.e., gloves).

1.6 Summary of Method

This automated method is based on the distillation of phenol and subsequent reactions of the distillate with alkaline ferricyanide and 4-aminoantipyrine to form a red complex which is measured at 505 nm.

1.7 Method Interferences

1.7.1 Background contamination from plastic tubing and samples containers is eliminated by filling the wash receptacle by siphon and using glass tubes for the samples and standards.

1.7.2 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of less than 4 with H_2SO_4 and aerating briefly by stirring.

1.7.3 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate. If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be low.

2.0 APPARATUS AND MATERIALS

2.1 Distillation apparatus, all glass, consisting of a 1 liter Pyrex distilling apparatus with Graham condenser.

2.2 Technicon AutoAnalyzer AAII, having:

2.2.1 Sampler.

2.2.2 Proportioning Pump.

2.2.3 Colorimeter equipped with a 50 mL flowcell and 505 nm filter.

2.2.4 Recorder.

2.2.5 Manifold.

2.3 Class A volumetric flasks - 100 mL.

2.4 500 mL graduated cylinders.

2.5 Class A pipets - 0.5, 1.0, 5.0 and 10.0 mL sizes.

2.6 Calibrated syringe - 1 mL.

2.7 Top loading balance.

2.8 500 mL Erlenmeyer flasks.

2.9 pH meter.

2.10 One liter flasks.

2.11 Glass sample vials.

2.12 Reagents

2.12.1 Buffered potassium ferricyanide: Dissolve 1.0 g of potassium ferricyanide, 1.55 g of boric acid and 1.875 g of potassium chloride in 400 mL of distilled water. Adjust pH to 10.3 with 1 N sodium hydroxide (Section 2.12.2) and dilute to 500 mL. Add 0.5 mL of Brij-35. Prepare fresh weekly.

2.12.2 Sodium hydroxide (NaOH), 1 N: Dissolve 40 g of NaOH in 500 mL of distilled water, cool and dilute to 1 liter.

2.12.3 4-Aminoantipyrine: Dissolve 0.325 g of 4-aminoantipyrine in 400 mL of distilled water and dilute to 500 mL. Prepare fresh daily.

2.12.4 Sulfuric Acid, H_2SO_4, concentrated.

2.12.5 Phenol Stock Standard solution, 1000 mg/L: Dissolve 1.00 g of phenol into 1 liter of distilled water. Add 0.5 mL of concentrated sulfuric acid as a preservative.

2.12.6 Phenol Control Standard solution, 1000 mg/L: Dissolve 1.00 g of phenol into 1 liter of distilled water. Add 0.5 mL of concentrated sulfuric acid as a preservative.

NOTE: It is recommended that this solid phenol reagent be obtained from a different source supplier than the phenol used for making the Stock Phenol Solution (Section 2.12.5). However, if the solid phenol reagent to be used is obtained from the same manufacturer, it must be from a different lot than the Stock Phenol Solution.

2.12.7 Intermediate Phenol Standard solution, 10 mg/L: Dilute 10 mL of the Phenol Stock Standard (Section 2.12.5) into 1 liter.

2.12.8 Intermediate Phenol Control solution, 10 mg/L: Dilute 10 mL of the Phenol Control Standard (Section 2.12.6) into 1 liter.

2.12.9 Calibration Standards: Prepare a series of standards by pipeting the following volumes of the Intermediate Phenol Standard solution (Section 2.12.7) into a series of 100 mL volumetric flasks. Prepared fresh daily.

Volume of Intermediate Phenol Standard (mL)	Concentration of Phenol Standard (ug/L)
0.0	0.0
0.02	2.0
0.05	5.0
0.10	10.0
0.25	25.0
0.50	50.0
1.00	100.0

3.0 SAMPLE HANDLING AND STORAGE

3.1 Sampling Procedure - Samples for phenols analysis shall be placed in cleaned, wide-mouthed, glass jar with a Teflon lined lid. Sample jars shall be placed in a temperature-controlled [4°C] chest immediately following sampling and delivered to the laboratory as soon as possible.

3.2 Container - The sampling container used is a 1 L wide mouthed glass container with a teflon lined cap.

3.3 Storage Conditions - Samples are kept on ice in coolers until shipped to the analytical lab. Upon arrival, the samples are stored at 4°C.

3.4 Holding Time Limits - The holding time for soil samples is 28 days from the time of sampling to time of analysis.

3.5 Solution Verification - Calibration solutions are verified with the analysis of the daily control spikes and references. Spiking solutions are prepared monthly and are verified prior to used by comparison to the calibration standards. All standard spike solutions are maintained at 4°C.

4.0 CALIBRATION

4.1 Initial Calibration

The instrument is standardized by analyzing the calibration standards specified in Section 2.12.9 and a blank. The absorbance is read at 505 nm and the peak heights are read off the strip chart recorder. The linear regression equation is determined for concentration versus response.

4.2 Calibration Checks

4.2.1 Calibration Check Standard/Initial Calibration Verification (ICV) - An ICV must be analyzed after the calibration standards. The ICV is prepared from a different source than the Stock or Control Standards, if available, or from the same source as the Control standard but prepared on a different day and/or by a different analyst from the Control standard. The concentration of the ICV is 50 ug/L. The acceptance criteria of the ICV is $\pm$ 15 % of the known concentration.

4.2.2 Continuing Calibration Verification Standard - A Continuing Calibration Verification Standard (CCV) must be analyzed after every ten (10) samples and at the end of analysis. The CCV is the 50 ug/L standard. The recovery based on the standard curve must be within 15 % of the known value.

4.2.3 If the recovery of the reference standard or CCV does not meet the acceptance criteria, the standard must be rerun. If either standard still fails, the samples analyzed since the last acceptable reference standard or CCV must be rerun. If the samples are reanalyzed and the CCV still fails, then your Department Manager and the Laboratory Coordinator must be notified. The Laboratory Coordinator will notify USACE to determine further action.

4.3 Daily Calibration

For daily calibration, an initial calibration curve and QC checks will be performed as indicated in Sections 4.1 and 4.2.

5.0 PROCEDURE

Daily control spike samples (Section 7.3) and environmental samples are prepared and analyzed as follows:

5.1 Distillation

5.1.1 Measure 1 g of a soil sample into the distillation apparatus and add 500 mL of Type I water. Check that the pH is less than 4. If pH is greater than 4, adjust the pH with H_2SO_4.

5.1.2 Distill 450 mL of sample, stop the distillation, and when boiling ceases add 50 mL of warm distilled water to the flask and resume distillation until 500 mL have been collected.

5.2 Chemical Reactions - Phenolic compounds react with 4-aminoantipyrine (4AAP) in the presence of potassium ferricyanide at a pH of 10 to form a stable red complex which is measured at 505 nm.

5.3 Instrument Analysis

5.3.1 Set up the manifold as shown in Attachment A.

5.3.2 Fill the wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 liter/hr).

5.3.3 Set Cam to 20 1/2. Allow the colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Use polyethylene tubing for sample line. When new tubing is used, about 2 hours may be required to obtain a stable baseline. This two hour period may be necessary to remove the residual phenol from the tubing.

5.3.4 Analyze the calibration standards in order of increasing concentration.

5.3.5 Analyze the daily quality control samples and reference sample.

5.3.6 Analyze the samples. Be sure to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) after every 10 samples.

5.3.7 Dilute samples that have concentrations exceeding the upper standard range and reanalyze.

5.3.8 End the run with a CCV and CCB to ensure that instruments have maintained stability throughout the run.

6.0 CALCULATION

6.1 Measure the peak height of each of the calibration standards and record the peak height on the chromatogram and on the run log. Develop a linear regression fit for the standards by relating concentration to peak height. Verify that the correlation curve of the curve ≥ 0.995.

6.2 Measure the peak height of each sample and quality control standard. Apply the linear regression equation, developed in Section 6.1, to the peak heights obtained to determine the concentration of ammonia.

6.3 To determine the concentration of phenol in the original sample the following example equation should be used:

$$\text{Sample conc.} = \frac{\text{Curve conc. x Dilution Factor x Final Distillation Volume}}{\text{Sample Weight x \% moisture}}$$

6.4 Method blank data with a response of less than the low standard should be entered into CLASS™ as 0 response, status = final. The actual response will be entered for any method blank with a response equal to or greater than that of the low standard.

7.0 QUALITY CONTROL

7.1 A Method blank (MB) must be analyzed with every lot. The MB consists of 1 g of AEC standard soil and 500 mL of Type I water. Follow the same procedure as the samples.

7.2 A Continuing Calibration Blank (CCB) must be analyzed after every 10 samples. The CCB is Type I water.

7.3 The following daily control spike samples are prepared by adding the following volumes of the intermediate control stock (Section 2.12.8) to 1 g of AEC standard soil in 500 mL of Type I water. Follow the same procedure as the samples.

Daily Control Spike Sample Prepared	Volume (mL) of AEC Intermediate Spike Solution Spiked into 1 g	Concentration of Control Spike Solution (ug/g)
Blank	0	0
Low	0.2	2.0
High	2.0	20.0
High	2.0	20.0

7.4 The Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) are not required for AEC projects, but will be analyzed if required by the contract or project. The SPM and SPMD are made by pipeting 2.5 mL of the 10 mg/L Intermediate Phenol Control solution (Section 2.12.8) into 1 g. Spiking into the matrix must be done prior to distillation and analysis. The spiking concentration must be within the concentration range of the calibration standards.

7.5 Control Charts

7.5.1 Data from spiked QC samples, within a lot, will be compared to control chart limits to demonstrate that analysis of the lot are under control. Control charts are prepared for each target analyte using percent recovery data from the spiked QC samples (low and high level).

$$\% \text{ Recovery} = \frac{\text{Found Concentration - Method Blank}}{\text{Spiked Concentration}} \times 100$$

7.5.2 To prepare control charts, the analyst will submit a data batch including spike and method blank samples to Information Services after analysis. Information Services will put the information into the USAEC control chart program. The following control charts will be returned to the analysts.

7.5.2.1 Average (x) percent recovery for the two high concentration spiked QC samples in each lot,

7.5.2.2 Difference (R) between the percent recoveries for the two high concentration spiked QC samples in each lot,

7.5.2.3 Three-point moving average (x) spike recovery of the low-concentration spike QC sample, and

7.5.2.4 Three-point moving difference (R) between the percent recoveries for the low-concentration spike QC sample.

7.5.3 The average (x), average range (R) and control limits for x and R shall be updated after each lot for the first 20 in control lots. Limits established after Lot 20 will be used for the next 20 lots. Control charts will be updated after each 20 in control lots thereafter using the most recent 40 lots of QC data. In updating the control charts, the new data must be combined with the individual values of previous percent recoveries and not the mean of all previous data.

8.0 REFERENCES

8.1 Test Methods for Evaluating Solid Waste, (EPA Method 9066A) EPA-SW-846, 3rd Edition, September 1986.

8.2 Standard Methods for the Examination of Water and Wastewater, 17^{th} Edition, 1989.

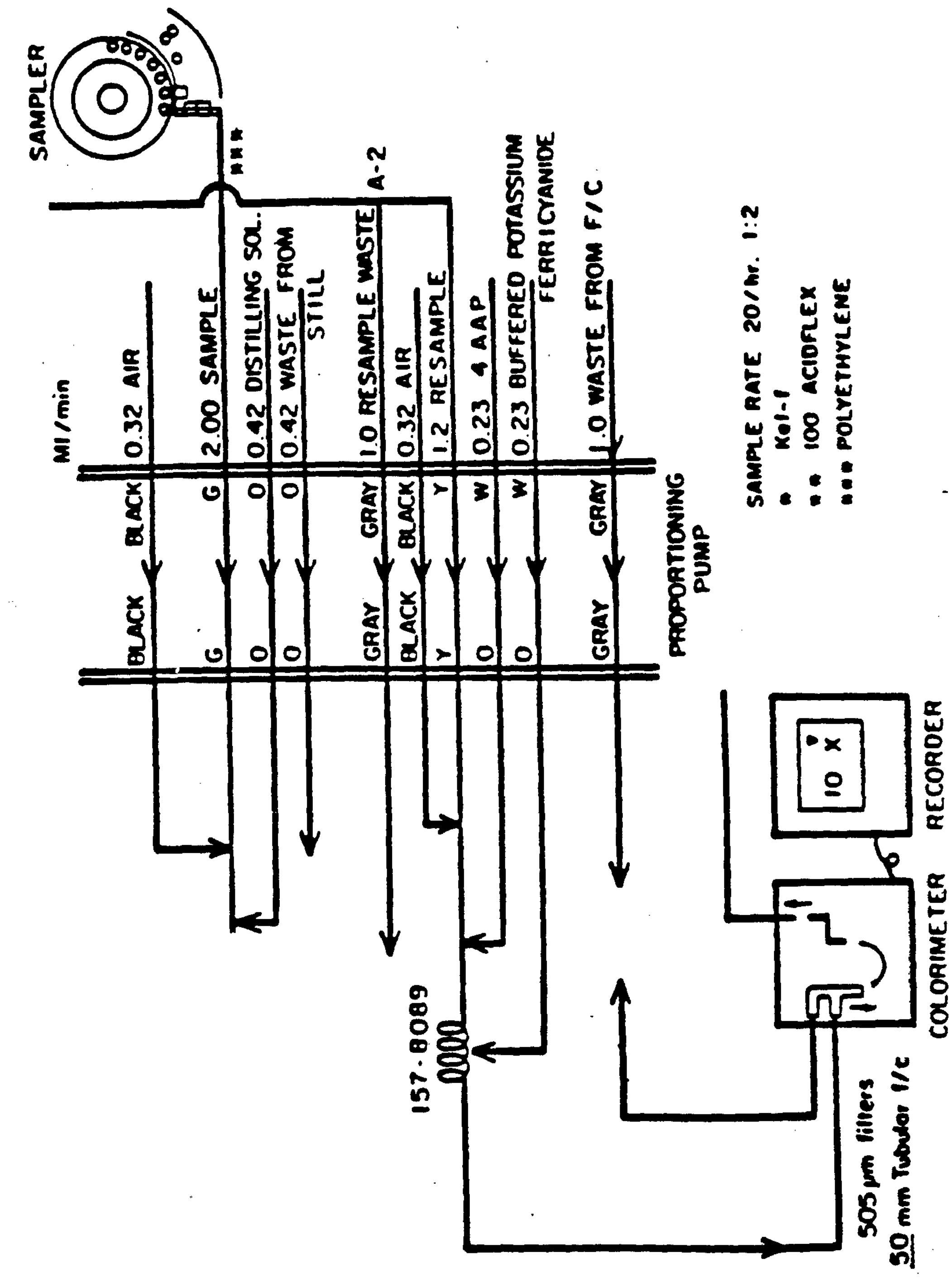
9.0 ATTACHMENTS

9.1 Attachment A - **AUTOANALYZER SCHEMATIC**

9.2 Attachment B - **TYPICAL TECHNICON RUN SEQUENCE**

9.3 Attachment C - **METHOD DETECTION LIMIT STUDY**

9.4 Attachment D - **DEVIATION FROM METHOD 9066**


SAMPLER
A-2
Ml/min
0.32 AIR
2.00 SAMPLE
0.42 DISTILLING SOL.
0.42 WASTE FROM STILL
1.0 RESAMPLE WASTE
0.32 AIR
1.2 RESAMPLE
0.23 4 AAP
0.23 BUFFERED POTASSIUM FERRICYANIDE
1.0 WASTE FROM F/C
BLACK
G
O
O
GRAY
BLACK
Y
W
W
GRAY
BLACK
G
O
O
GRAY
BLACK
Y
O
O
GRAY
PROPORTIONING PUMP
SAMPLE RATE 20/hr. 1:2
* Kel-f
** 100 ACIDFLEX
*** POLYETHYLENE
10 X
RECORDER
COLORIMETER
157-B089
505 μm filters
50 mm Tubular f/c

Attachment B - TYPICAL TECHNICON RUN SEQUENCE

High standard to check instrument range	
Blank	
Standard 1 (MDL)	
Standard 2	
Standard 3	
Standard 4	
Standard 5	
Standard 6	
Initial calibration blank - ICB	
Initial calibration verification - ICV (reference)	±15 %
Method blank (prep blank)	
Low Spike - SP1	
High Spike - SP2	
High Spike - SP3	
Sample #1	
Sample #1 matrix spike	
Sample #1 matrix spike duplicate	
Sample #2	
Sample #3	
Sample #4	
Continuing calibration blank - CCB	
Continuing calibration verification - CCV	± 15%
Sample #5	
.	
.	
.	
Sample #14	
CCB	
CCV	± 15%
Sample #15	
.	
.	
.	
Sample #24	
CCB	
CCV	± 15%
.	

Attachment C - METHOD DETECTION STUDY

METHOD DETECTION LIMIT STUDY

Laboratory Name: Environmental Science & Engineering, Inc. (ESE)
Address: P.O. Box 1703, Gainesville, Florida, 32602-1703
Manager: Dr. John J. Mousa, Director, Gainesville Laboratory
Phone: (904) 332-3318

Method: Phenols in Soil (Modified 9066A)

Compound Name	R1 (ug/kg)	R2 (ug/kg)	R3 (ug/kg)	R4 (ug/kg)	R5 (ug/kg)	R6 (ug/kg)	R7 (ug/kg)	X (ug/kg)	S	MDL (ug/kg)
Phenols	4860	4580	4540	4470	4320	4350	4280	4486	185	629

Note: Target concentration for Phenols in soil is approximately 5000 ug/kg
Actual target concentrations vary due to varying extract volumes.

R = Actual concentration for each replicate 1-7
X = Average concentration
S = Standard deviation
ug/kg = microgram per kilogram

Attachment D - **DEVIATION FROM METHOD 9066A**

1. SW-846 Method 9066A uses an automated continuous-flow analytical instrument with attached distillation apparatus and heating bath with distillation coil. ESE's Technicon AAII is not equipped with an attached distillation apparatus and heating bath with distillation coil. Hence, sample distillation is performed separately from analysis using an all glass distillation apparatus consisting of a 1 liter Pyrex distilling apparatus with Graham condenser.

2. Calibration standards are prepared daily and used only on the day standards are prepared. Therefore, the calibration standards are not preserved with 2 drops of concentrated sulfuric acid as required by SW-846 Method 9066A.

3. Soil and sediment matrices are not included in the scope of SW-846 Method 9066A. Therefore, SW-846 Method 9066A has been modified for inclusion of soil and sediment samples in the method. The modifications made are only on the distillation procedure which are as follows:

   One gram of a soil sample is used.

   A 500 mL volume of Type I water is added to the soil sample, along with enough sulfuric acid to ensure that the pH is 4 or less.

   The distillation and analysis procedure defined in the SW-846 method is then followed as written with no further deviations.

4. Method 9066A states that a calibration curve should be analyzed every twelve hours of continous sample analysis. A continuing calibration check is run every ten samples (approximately every 1/2 hour). Continuous run times seldom exceed 4-8 hours. Method 9066 states that a calibration curve should be analyzed every hour (three point curve and a blank). The continuing calibration check every 10 samples has proven that calibration stability is maintained and calibration every hour is an excessive requirement.

2/11/93
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SOP-AS$\emptyset$3231-007
Revision 0
Date 07/01/92

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **pH IN WATER (EPA METHOD 150.1)**

Effective Date: 9/8/92

Prepared by: Kathleen K. Allen 9/4/92

Reviewed by: Kenneth U. Erondu Kenneth U. Erondu 9/4/92

Approved by: John J. Mousa John J. Mousa 9/8/92
(Gainesville Laboratory Director)

TABLE OF CONTENTS

TITLE: **pH IN WATER (EPA Method 150.1)**

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a consistent method for determination of pH in water.

2.0 SCOPE

This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition).

3.0 SUMMARY OF METHOD

The pH of a sample is determined electrometrically using a combination electrode.

4.0 METHOD INTERFERENCES

4.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10.0, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1.0 may give incorrectly high pH measurements.

4.2 Temperature fluctuations will cause measurement errors.

4.3 Errors will occur when the electrodes become coated with any type of adhering substance (i.e., oil, particles). If this occurs, rinse the electrode thoroughly. If this is not sufficient to clean the electrode, place it in an ultrasonic bath, or in 1:1 HCl so that the lower third of the electrode is submerged, and then thoroughly rinse with water.

5.0 APPARATUS AND MATERIALS

5.1 pH meter with temperature sensor for automatic compensation.

5.2 Electrodes:

5.2.1 Glass electrode in combination with a calomel reference electrode, or

5.2.2 Combination electrode.

5.3 Beaker: 50 ml.

6.0 REAGENTS

6.1 Deionized (DI) water.

6.2 Standard buffer solutions at pH of 4,7 and 10 which are available from a commercial vendor.

6.3 Electrode internal solution, 3 M KCL solution.

7.0 PROCEDURE

7.1 Calibration

7.1.1 Check the temperature of the pH 7 buffer that is used to calibrate the meter and turn temperature knob to that temperature.

7.1.2 Turn the function knob from standby to pH mode. Lower the electrode into the pH 7 buffer and adjust the CALIBRATE knob so that the pH meter reads 7.00.

7.1.3 Raise the electrode, and rinse with distilled water. Repeat this procedure after each use of the electrode.

7.1.4 Lower the electrode into the pH 4 buffer and adjust the SLOPE knob until the meter reads 4.00. Clean electrode as in step 7.1.3.

7.1.5 Lower the electrode into pH 10 buffer and record the pH reading. A reading of 10 ± 0.05 indicates that the electrode is properly calibrated. Clean electrode as in step 7.1.3.

7.1.6 A reading outside of 10 ± 0.05 indicates that the electrode has been calibrated improperly, and the following actions may need to be taken.

7.1.6.1 Get a new bottle of pH 10 buffer and check the pH. If the new pH buffer solution gives a reading within 10 ± 0.05, then perform sample analysis.

7.1.6.2 If the new bottle of pH 10 buffer solution is outside of criteria, the meter may have been incorrectly calibrated from the pH 7 buffer. Check original calibration with new pH 7 buffer solution and re-calibrate, if necessary, following steps 7.1.2 through 7.1.5.

7.1.6.3 If steps 7.1.6.1 and 7.1.6.2 does not correct the problem, clean the pH probe and check the pH probe internal solution. The internal solution may need to be changed.

7.1.6.4 If steps 7.1.6.1 through 7.1.6.3 does not correct the problem, check with the Water Quality Department Manager.

7.2 Sample analysis

7.2.1 Pour enough sample into a clean beaker to cover the sensing element of the pH probe. Lower the electrode into the sample and carefully swirl to mix sample. Measure and record the pH.

7.2.2 Rinse the electrode as in step 7.1.3 and repeat measurements on successive volumes of the sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient

7.2.3 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.2.4 Report the pH to the nearest 0.1 unit.

8.0 QUALITY CONTROL

8.1 Method blanks (MB) must be analyzed at a frequency of 5% for every analytical batch unless specified differently by a project. MB consists of deionized (DI) water.

8.2 Replicate samples must be analyzed at a frequency of 5% for every analytical batch unless specified differently by a project.

Note: The actual number of QC required is rounded up to the nearest whole number, i.e., 5% = 1 QC for 1-20 samples; 2 QC for 21-40 samples, etc.

9.0 REFERENCE

9.1 Methods for Chemical Analysis of Water and Wastes (EPA 150.1), EPA 600/4-79-020, revised March 1983.

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: pH IN SOIL (EPA METHOD 9045)

Effective Date: 9/8/92

Prepared by: Kathleen K. Allen ________ 9/4/92

Reviewed by: Kenneth U. Erondu Kenneth U. Erondu 9/4/92

Approved by: John J. Mousa JJMousa 9/8/92
(Gainesville Laboratory Director)

TABLE OF CONTENTS

TITLE: pH IN SOIL (EPA Method 9045)

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a consistent method for the determination of pH in noncalcareous soil.

2.0 SCOPE

This method is an electrometric procedure which has been approved for measuring pH in noncalcareous soils and wastes.

3.0 SUMMARY OF METHOD

The soil sample is mixed with deionized water and the pH of the supernatant is measured with a pH meter.

4.0 METHOD INTERFERENCES

4.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10.0, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1.0 may give incorrectly high pH measurements.

4.2 Temperature fluctuations will cause measurement errors.

4.3 Errors will occur when the electrodes become coated with any type of adhering substance (i.e., oil, particles). If this occurs, rinse the electrode thoroughly. If this is not sufficient to clean the electrode, place it in an ultrasonic bath, or in 1:1 HCl so that the lower third of the electrode is submerged, and then thoroughly rinse with water.

5.0 APPARATUS AND MATERIALS

5.1 pH meter with temperature sensor for automatic compensation.

5.2 Electrodes:

5.2.1 Glass electrode in combination with a calomel reference electrode, or

5.2.2 Combination electrode.

5.3 Beaker: 50 ml.

6.0 REAGENTS

6.1 Deionized (DI) Water.

6.2 Standard buffer solutions at pH of 4,7 and 10 which are available from a commercial vendor.

6.3 Electrode internal solution, 3 M KCL solution.

7.0 PROCEDURE

7.1 Calibration

7.1.1 Check the temperature of the pH 7 buffer that is used to calibrate the meter and turn temperature knob to that temperature.

7.1.2 Turn the function knob from standby to pH mode. Lower the electrode into the pH 7 buffer and adjust the CALIBRATE knob so that the pH meter reads 7.00.

7.1.3 Raise the electrode, and rinse with distilled water. Repeat this procedure after each use of the electrode.

7.1.4 Lower the electrode into the pH 4 buffer and adjust the SLOPE knob until the meter reads 4.00. Clean the electrode as in 7.1.3.

7.1.5 Lower the electrode into the pH 10 buffer and record the pH reading. A reading of 10 ± 0.05 indicates that the electrode is properly calibrated. Clean the electrode as in step 7.1.3.

7.1.6 A reading outside of 10 ± 0.05 indicates that the electrode has been calibrated improperly, and the following actions may need to be taken.

7.1.6.1 Get a new bottle of pH 10 buffer and check the pH. If the new pH buffer solution gives a reading within 10 ± 0.05, then perform sample analysis.

7.1.6.2 If the new bottle of pH 10 buffer solution is outside of criteria, the meter may have been incorrectly calibrated from the pH 7 buffer. Check original calibration with new pH 7 buffer and re-calibrate, if necessary, following steps 7.1.2 through 7.1.5.

7.1.6.3 If steps 7.1.6.1 and 7.1.6.2 does not correct the problem, clean the pH probe and check the pH probe internal solution. The internal solution may need to be changed.

7.1.6.4 If steps 7.1.6.1 through 7.1.6.3 does not correct the problem, check with the Water Quality Department Manager.

7.2 Sample preparation and analysis

7.2.1 Weigh 20g of soil in a 50 ml beaker. Add 20 mL of DI water and stir the suspension several times during the next 30 minutes.

7.2.2 Let the suspension settle for approximately one hour to allow the suspended clay to settle out.

7.2.3 Lower the electrode into the suspension until the electrode is in the supernatant solution. Measure and record the pH of the sample. Rinse the electrode as in step 7.1.3. and repeat measurements on successive volumes of the sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient

7.2.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.2.5 Report the results as "soil pH measured in water".

8.0 QUALITY CONTROL

8.1 Method blanks (MB) must be analyzed at a frequency of 5% for every analytical batch unless specified differently by a project. MB consists of deionized (DI) water.

8.2 Replicate samples must be analyzed at a frequency of 5% for every analytical batch unless specified differently by a project.

Note: The actual number of QC required is rounded up to the nearest whole number, i.e., 5% = 1 QC for 1-20 samples; 2 QC for 21-40 samples, etc.

9.0 REFERENCES

9.1 Test Methods for Evaluating Solid Waste (EPA 9045), EPA-SW846, 3rd Edition, September 1986.

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **CONDUCTANCE (EPA METHOD 120.1)**

Effective Date: 1/8/93

Prepared by:	Kathleen K. Allen	[signature]	1/4/93
Reviewed by:	Kenneth U. Erondu	[signature]	12/31/92
Approved by: (Gainesville Laboratory Director)	John J. Mousa	[signature]	1/8/93

TABLE OF CONTENTS

TITLE: CONDUCTANCE (EPA METHOD 120.1)

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a consistent method for the determination of conductivity of water samples.

2.0 SCOPE

This method is applicable to drinking, surface and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition).

3.0 SUMMARY OF METHOD

3.1 The specific conductance of a sample is measured by the use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.

3.2 Samples are preferably analyzed at 25° C. If not, temperature corrections are made and results reported at 25° C.

4.0 METHOD INTERFERENCE

4.1 Temperature variations and corrections represent the largest source of potential error.

4.2 If analysis is not completed within 24 hours of sample collection, sample should be filtered through a 0.45 micron filter and stored at 4° C. Filter and apparatus must be washed with high quality distilled water and pre-rinsed with sample before use.

5.0 APPARATUS AND MATERIALS

5.1 Conductivity bridge, range 1 to 1000 μmho per centimeter with automatic temperature correction capabilities.

5.2 Conductivity cell, cell constant 1.0 or equivalent. YSI #3403 or equivalent.

6.0 REAGENTS

6.1 Standard potassium chloride solution, (KCl) 0.01 M: 0.7456 g of pre-dried (2 hours at 105° C) KCL is dissolved in distilled water and diluted to 1 liter at 25° C.

6.2 Standard potassium chloride solution, 0.1 M: 7.456 g of pre-dried (2 hours at 105° C) KCL is dissolved in distilled water and diluted to 1 liter at 25° C.

7.0 PROCEDURE

7.1 Check instrument calibration using the 0.01 M (Section 6.1) and the 0.1 M (Section 6.2) KCL solutions.

7.1.1 The 0.01 M KCL solution should give a conductivity reading of 1413 μmhos $\pm$ 1 % .

7.1.2 The 0.1 M KCL solution should give a conductivity reading of 12,900 $\pm$ 1%.

7.1.3 If the calibration standard solutions do not give a conductivity reading within the acceptable criteria, remake the calibration standards.

7.1.4 If the new calibration standard solutions do not give a conductivity reading within the acceptable criteria, clean the conductivity cell following the manufacturers instructions.

7.1.5 If cleaning the conductivity cell does not give a conductivity reading within the acceptable criteria, see Water Quality supervisor. The conductivity cell may need to be replaced.

7.2 Allow samples to come to room temperature, if possible.

7.3 Pour enough sample into a teflon beaker to cover the conductivity cell.

7.4 Adjust range switch to get a reading with three significant figures. Record the conductivity reading and range.

8.0 CALCULATION

Report results as specific conductance, μmhos/cm at 25° C.

9.0 QUALITY CONTROL

9.1 Method blanks (MB) must be analyzed at a frequency of 5% for every analytical batch unless specified differently by a project. MB consists of deionized (DI) water.

9.2 Replicate samples must be analyzed at a frequency of 5% for every analytical batch unless specified differently by a project.

Note: The actual number of QC required is rounded up to the nearest whole number, i.e., 5% = 1 QC for 1-20 samples; 2 QC for 21-40 samples, etc.

10.0 REFERENCE

Methods for Chemical Analysis of Water and Wastes (EPA 120.1), EPA-600/4-79-020, Revised March 1983.

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **TOTAL ORGANIC CARBON (TOC) IN WATER (EPA METHOD 415.1)**

Effective Date: 10/16/92

Prepared by: Kathleen K. Allen 10/15/92

Reviewed by: Kenneth U. Erondu 10/15/92

Approved by: John J. Mousa 10/16/92
(Gainesville Laboratory Director)

TABLE OF CONTENTS

TITLE: TOTAL ORGANIC CARBON (TOC) IN WATER (EPA METHOD 415.1)

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a consistent method for the determination of total organic carbon in water samples.

2.0 SCOPE

2.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes.

2.2 Detection limit for this method is 1.0 mg/L.

2.3 This procedure is applicable only to homogeneous samples which can be drawn into the apparatus reproducibly by means of the autosampler.

3.0 SUMMARY OF METHOD

Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed is measured directly by a non-dispersive infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample.

4.0 METHOD INTERFERENCES

Removal of carbonate and bicarbonate by acidification and purging with purified gas will result in the loss of volatile organic substances.

5.0 APPARATUS AND MATERIALS

5.1 Dohrmann DC-190 High Temperature Total Organic Carbon (TOC) Analyzer with autosampler.

5.2 8 mL autosampler vials.

6.0 REAGENTS

6.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank.

6.2 Potassium Hydrogen Phthalate, Stock Standard, 2000 mg carbon/L: Dissolve 0.4256 g of potassium hydrogen phthalate (primary standard grade) in distilled water and dilute to 100.0 mL. This solution expires in thirty days.

6.3 Potassium Hydrogen Phthalate, Control Stock Standard, 2000 mg carbon/L: Dissolve 0.4256 g of potassium hydrogn phthalate (primary standard grade) in distilled water and dilute to 100.0 mL. This solution expires in thirty days.

NOTE: It is recommended that these chemicals be obtained from a different supplier than the chemicals used to make the Stock Standard (Section 6.2). However, if the chemicals are obtained from the same manufacturer, they must be from different lots than the chemicals used to prepare the Stock Standard.

6.4 Preparation of Calibration Standards: Prepare a series of standards by pipeting the appropriate volumes of the 2000 mg carbon/L stock standard (Section 6.2), into a series of 100 mL volumetric flasks and dilute to volume with distilled water. It is recommended that the following volumes of the 2000 mg carbon/L stock standard be used to obtain a working curve of approximately 1 - 100 mg/L.

Volume of 2000 mg/L Stock Standard used (mL)	Concentration (mg/L)
0.05	1.0
0.125	2.5
0.25	5.0
0.5	10.0
1.5	30.0
5.0	100.0

These standards are to be made fresh daily.

6.5 Intermediate Control Stock Standard: Prepare a 20 mg carbon/L intermediate control stock by pipetting 1 mL of Control Stock Standard (Section 6.3) into a 100 mL volumetric flask. Bring to volume with distilled water. This solution is to be made fresh daily.

7.0 PROCEDURE

7.1 Analyze the calibration standards in order of increasing concentration. All standard concentrations should be within $\pm$ 10% of stated concentration. If the standards are outside of this criteria, the instrument must be re-calibrated. To calibrate the instrument, analyze one standard in duplicate, preferably the midpoint standard (and follow by analyzing distilled water). Press the calibration button and re-analyze all calibration standards to ensure that the instrument is properly calibrated.

7.2 All samples, standards and QC aliquots should be run in duplicate with the instrument set to print averages for total carbon, inorganic carbon and organic carbon.

8.0 CALCULATIONS

The DC 190 Carbon Analyzer provides a printout showing all injections and averages for total carbon, inorganic carbon and organic carbon. This strip chart is to be included in the data batch along with a xerox copy of the instrument run log.

9.0 QUALITY CONTROL

9.1 Method blanks (MB) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. The MB consists of distilled water.

9.2 Standard Spike (SP) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. Use the 20 mg carbon/L Intermediate Control Stock Standard (Section 6.5) as the SP.

9.3 Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. SPM and SPMD are prepared by making a 1:1 dilution of the sample and the 20 mg carbon/L Intermediate Control Stock Standard.

NOTE: The actual number of QC required is rounded up to the nearest whole number, i.e., 5% = 1 QC for 1-20 samples; 2 QC for 21-40 samples, etc.

9.4 The Initial Calibration Verfication (ICV) is a quality control check used to ensure the validity of the calibration standards prior to running any samples. This requires that the ICV be prepared from the Control Stock Standard (Section 6.3). The concentration of the ICV must be within the range of the calibration standards; however, it is recommended that the concentration be approximately the same as the midpoint standard (Section 6.4).

(Alternatively, an EPA reference solution may be used.) SP

9.5 The Continuing Calibration Verification (CCV) is a quality control check used to ensure the validity of the curve while running samples. The CCV is the re-analysis of one of the original calibration standards. It is recommended that the midpoint standard be used.

10.0 REFERENCE

Methods for Chemical Analysis of Water and Wastes, (EPA method 415.1) EPA-600/4-79-020, Revised March 1983.

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **BIOLOGICAL OXYGEN DEMAND (EPA METHOD 405.1)**

Effective Date: 9/28/92

Prepared by: Kathleen K. Allen 9/23/92

Reviewed by: Kenneth U. Erondu Kenneth U. E 9/22/92

Approved by: John J. Mousa John J Mousa 9/28/92
(Gainesville Laboratory Director)

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TITLE: BIOLOGICAL OXYGEN DEMAND (EPA METHOD 405.1)

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a consistent method for the determination of biological oxygen demand.

2.0 SCOPE

2.1 The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewater. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria for the design of wastewater treatment plants.

2.2 The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20° C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

2.3 The detection limit for this method is 1 mg/L.

3.0 SUMMARY OF METHOD

The sample of waste, or an appropriate dilution, is incubated for 5 days at 20° C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

4.0 METHOD INTERFERENCES

Biological treatment plant effluents may contain significant numbers of nitrifying organisms. Because oxidation of nitrogenous compounds increases oxygen content, nitrification inhibition in this type of sample is recommended.

5.0 APPARATUS AND MATERIALS

5.1 Incubation bottles: 300 ml capacity with ground-glass stoppers. To prevent against air being drawn into the bottle during incubation, use a water seal for each bottle. Place a plastic cup over the mouth of the sealed bottle to prevent evaporation during incubation.

5.2 YSI oxygen probe.

5.3 YSI oxygen meter.

5.4 BOD incubator, 20 $\pm$ 1° C.

6.0 REAGENTS

6.1 Glucose-glutamic acid spike solution: Dry reagent - grade glucose and reagent - grade glutamic acid at 103° C for 1 hour. For BOD determinations not requiring an adapted seed, use a mixture of 150 mg glucose and 150 mg of glutamic acid diluted to 1 liter.

6.2 Dilution water: Open a Hach Nutrient Pillow (commercially available) and pour contents into dilution water container. Add 6 liters of DI water and shake to ensure adequate dissolved oxygen (8.5 mg/L).

6.3 Sodium Sulfite Solution, 0.025N: Weigh out 1.575 grams of Na_2SO_3 in a 1 liter volumetric flask and bring to mark with DI water.

6.4 Seeding solution, commercially available: Place one capsule full of dehydrated seed into 500 mls of dilution water and stir for 30 minutes.

7.0 PROCEDURE

7.1 Instrument Calibration

7.1.1 Place BOD probe into a BOD bottle 1/2 full of DI water and place on an insulated stir plate.

7.1.2 Turn on stir plate and the probe wiggler. The instrument should also be turned on at this time. Allow 15 - 20 minutes for the instrument to stabilize.

7.1.3 With the knob on 'ZERO' adjust the red needle to read 0 mg/L.

7.1.4 Switch the knob to 'FULL SCALE' and adjust the red needle to 15 mg/L.

7.1.5 Switch the knob to 'CALIB O2' and adjust the red needle to the appropriate SEA LEVEL for the area.

7.2 Sample Preparation

7.2.1 For each sample a series of dilutions should be made. All samples must be at room temperature before they are setup. Decide what dilutions are to be used on the samples and label the BOD bottles accordingly. Be sure to place a method blank at the beginning of the run and one at the end of the run. If the samples are known to be of a certain BOD range, 1 to 3 dilutions may be set up. If the range is unknown, 3 to 5 dilutions covering the broadest range of possible values is called for. Dilutions that deplete between 30 and 70% of the initial DO are the best to use for calculations. The following can be used as a guide for BOD ranges encompassed by various dilutions.

mls of sample in a 300 ml bottle	BOD range covered
200	3.0 - 9.8
100	6.0 - 19.0
50	12 - 39
25	24 - 78
15	40 - 130

8	75 - 244
4	150 - 488
2	300 - 975
1	600 - 1950
0.5	1200 - 3900

7.2.2 After adding the appropriate amount of sample (depending on the selected dilutions) fill the bottles to the top with seeded, if necessary, dilution water.

7.2.3 Rap the sides of the bottles with a solid glass stopper to dislodge any trapped air bubbles.

7.3 Sample analysis

7.3.1 Insert probe into the beginning method blank, turn knob to 'READ TEMP AND SET DIAL'. Read temperature from the bottom row and set dial to that temperature. Switch knob to 'READ O2' and wait for the instrument to stabilize, record reading in the logbook under initial DO.

7.3.2 Read and record each sample bottle label, temperature and the initial DO in the logbook.

7.3.3 Place a ground glass stopper into the top to make sure that there are no air bubbles or pockets present. If there are air bubbles or pockets add more dilution water. Insert stopper by putting a small amount of water into the depression around the stopper and cap with the plastic cap.

7.3.4 Place BOD bottles in the incubator at 20 $\pm$ 1° C for 5 days.

7.3.5 At the end of 5 days remove samples from the incubator, calibrate instrument as described in Section 7.1 and record the final DO and temperature using the procedure in Section 7.3.1.

8.0 QUALITY CONTROL

8.1 A 2% dilution of the glucose-glutamic acid standard must be analyzed with every analytical batch. The 2% dilution of glucose-glutamic acid must have a 5-day DO value of 200 $\pm$ 37 mg/L. Reject any BOD determinations made with this dilution water that does not meet this criteria.

8.2 Method blanks (MB) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. Fill a 300 ml BOD bottle completely full with dilution water, and analyze the same way as the samples.

8.3 Standard Spike (SP) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. Pipette 6 mL of the glutamic acid - glucose solution into each of the 300 mL BOD bottles, and then fill with dilution water. Analyze the same way as the samples.

8.4 Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. Pipette 6 mls of the glutamic acid - glucose solution into each diluted sample, and analyze the same way as the samples.

Note: The actual number of QC required is rounded up to the nearest whole number, i.e., 5% = 1 QC for 1-20 samples; 2 QC for 21-40 samples, etc.

9.0 CALCULATIONS

$$\text{mg BOD/L} = \frac{300}{(\text{initial DO} - \text{final DO}) \times \text{mls of sample}}$$

10.0 REFERENCES

10.1 Methods for Chemical Analysis of Water and Wastes (EPA 405.1), EPA-600/4-79-020, revised March 1983.

10.1 Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

10.1 Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.

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Revision 1
Date 10/28/92
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Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: CHEMICAL OXYGEN DEMAND (COD) IN WATER (HACH 8000)

Effective Date: 11/10/92

Prepared by:	Kathleen K. Allen	[signature]	11/6/92
Reviewed by:	Kenneth U. Erondu	Kenneth U. Erondu	11/6/92
Approved by: (Gainesville Laboratory Director)	John J. Mousa	John J. Mousa	11/10/92

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TITLE: CHEMICAL OXYGEN DEMAND (COD) IN WATER (HACH 8000)

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a consistent method for the determination of chemical oxygen demand in water.

2.0 SCOPE

2.1 This method is applicable to the determination of low level and high level chemical oxygen demand (COD) in drinking, surface and saline waters, domestic and industrial wastes.

2.2 The COD method is used as a measure of the oxygen equivalent to the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. Oxidation of most organic compounds is 95 to 100% of the theoretical value.

3.0 SUMMARY OF METHOD

Organic and oxidizable inorganic substances in the sample are oxidized by potassium dichromate in 50% sulfuric acid solution at 150^0 C. Dichromate is consumed in the oxidation of the organic matter, and the COD is determined spectrophotometrically.

4.0 METHOD INTERFERENCES

4.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.

4.2 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine and estuarine samples.

5.0 APPARATUS AND MATERIALS

5.1 COD block digester, 150° C.

5.2 COD digestion vials with digest reagent, commercially available.

5.3 Spectrophotometer.

6.0 REAGENTS

6.1 COD Stock Spiking Solution: Dissolve 0.8512 g of potassium hydrogen phthalate (KHP) in 1000 mL DI water. This solution is equal to 1000 mg COD/L.

6.2 COD Intermediate Stock Spiking Solution: Dilute 10 mL of COD Stock Spiking Solution (Section 6.1) in 100 mL DI. This solution is equal to 100 mg COD/L.

7.0 PROCEDURE

7.1 Sample preparation.

7.1.1 Turn on the COD reactor to preheat to 150°C.

7.1.2 Wrap a COD digestion reagent vial of the desired range in a towel to prevent injury in case of breakage. Cautiously remove the cap and pipette 2 mL of sample into the vial. Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Cap vial tightly. Hold vial over a sink and shake to thoroughly mix the contents.

CAUTION: Vial will become very hot during mixing.

7.1.3 Place the vial in a preheated COD reactor with the plastic shield in place. Heat the vials for two hours at 150°C.

7.1.4 Remove the vials from the reactor and allow to cool for 30 to 40 minutes. Measure the COD using the spectrophotometer.

7.2 Spectrophotometer procedure:

7.2.1 Adjust the spectrophotometer wavelength to 420 nm for low level or 620 nm for high level determinations.

7.2.2 Cover the empty sample compartment with the cell cover or insert the empty Hach COD adapter and adjust the Zero control knob to exactly 0% transmittance.

7.2.3 Insert the method blank into the adapter until the vial rests against the bottom of the adapter. Insert the method blank and adapter into the cell holder. Line up the Hach label on the vial with that on the cell holder and cover the compartment. Adjust the Full Scale control to 35% transmittance for low level or 100% for high level.

7.2.4 Insert a treated sample into the adapter and place it into the cell holder. Line up the label on the vial with that on the cell holder and cover the compartment. Record the % transmittance.

8.0 QUALITY CONTROL

8.1 Method blanks (MB) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. MB consists of pipetting 2 mL of DI water into a COD vial and following the same procedure used for the samples.

8.2 Standard Matrix Spike (SP) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. High Level: Pipette 1 mL of DI water and 1 mL of the Stock Spiking solution (Section 6.1) into a 0-1500 range COD vial. The target for high level spikes is 500 mg/L. Low level: Pipette 1 mL of DI water and 1 mL of the Intermediate Stock solution (Section 6.2) into a 0-150 range COD vial. The target for low level spikes is 50 mg/L.

8.3 Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. High level: Pipette 1 mL of sample and 1 mL of the Stock Spiking solution (Section 6.1) into a 0-1500 range COD vial. The target

for high level matrix spikes is 1000 mg/L with a dilution of two. Low level: Pipette 1 mL of sample and 1 mL of Intermediate Spiking solution (Section 6.2) into a 0-150 range COD vial. The target for low level matrix spikes is 100 mg/L with a dilution of two.

9.0 CALCULATIONS

The mg/L COD is determined from Table 1 - High Range Calibration Table (Attachment A) or Table 2 - Low Range Calibration Table (Attachment B) by selecting the appropriate line from the "% T, Tens" column and the appropriate column from the "% T, Units" group of columns. For example, if the instrument reading was 46% T, the value where the 40% line and 6% column intersect will be the mg/L COD concentration. On the Low Range Table, the value obtained would be 38.4 mg/L.

10.0 REFERENCES

Procedures for Water and Wastewater Analysis, 2nd Edition, Hach Company, April 1987.

11.0 ATTACHMENTS

11.1 Attachment A - **TABLE 1, HIGH RANGE CALIBRATION TABLE, 1 - 1500 MG/L COD.**

11.2 Attachment B - **TABLE 2, LOW RANGE CALIBRATION TABLE, 1 - 150 MG/L COD.**

ATTACHMENT A

TABLE 1
High Range Calibration Table, 1-1500 mg/L COD
MG/L COD VS % TRANSMITTANCE
% T. Units

% T, Tens	0	1	2	3	4	5	6	7	8	9
0	--	--	--	--	--	--	--	--	--	--
10	--	--	--	--	--	--	--	--	--	--
20	--	--	1515	1468	1425	1385	1345	1308	1272	1238
30	1203	1170	1138	1107	1077	1048	1020	992	965	940
40	915	890	867	844	821	798	776	754	733	713
50	693	674	655	637	618	599	581	563	545	528
60	512	496	479	463	447	432	417	402	388	374
70	359	345	331	317	303	290	277	264	252	239
80	226	213	201	188	177	165	153	141	130	119
90	108	97	85	74	63	53	42	31	21	10

ATTACHMENT B

TABLE 2

Low Range Calibration Table, 1-150 mg/L COD

MG/L COD VS % TRANSMITTANCE

% T. Units

% T, Tens	0	1	2	3	4	5	6	7	8	9
10	--	--	--	--	--	--	--	--	--	--
20	--	--	--	--	--	--	--	--	--	--
30	--	--	--	--	--	0	3.7	7.5	11.3	15.0
40	18.7	22.2	25.6	28.9	32.1	35.3	38.4	41.4	44.4	47.3
50	50.2	53.0	55.8	58.5	61.2	63.8	66.3	68.8	71.3	73.8
60	76.2	78.6	80.9	83.2	85.5	87.7	89.9	92.1	94.2	96.3
70	98.4	100.4	102.4	104.3	106.2	108.2	110.1	112.0	113.9	115.8
80	117.6	119.4	121.1	122.8	124.5	126.2	127.9	129.6	131.2	132.8
90	134.5	136.1	137.7	139.3	140.9	142.5	144.1	145.6	147.0	148.6

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: ALKALINITY (EPA METHOD 310.1)

Effective Date:________________

Prepared by: Kathleen K. Allen ________ 1/4/93

Reviewed by: Kenneth U. Erondu ________ 12/31/92

Approved by: John J. Mousa ________ 1/8/93
(Gainesville Laboratory Director)

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TITLE: ALKALINITY (EPA METHOD 310.1)

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a consistent method for the determination of alkalinity as $CaCO_3$.

2.0 SCOPE

2.1 This method is applicable to drinking, surface and saline waters, domestic and industrial wastes.

2.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration greater than 50 mL.

2.3 Automated titrimetric analysis is equivalent.

3.0 SUMMARY OF METHOD

3.1 An unaltered sample is titrated to an electrometrically determined endpoint of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.

3.2 The detection limit for this method is 5.0 mg/L-$CaCO_3$.

4.0 METHOD INTERFERENCES

4.1 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the pH measurement.

4.2 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an end point of pH 3.9 using the procedure in: Annual book of ASTM Standards, part 31, "Water", p 115, D-1067, Method D.

4.3 Oil and grease, by coating the pH electrode, may also interfere, causing a

sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes.

5.0 APPARATUS AND MATERIALS

5.1 pH meter that can be read to 0.05 pH units.

5.2 Magnetic stirrer, pipets, flasks, and other standard laboratory equipment.

5.3 Burets, pyrex 50 mL.

6.0 REAGENTS

6.1 Sodium carbonate solution, approximately 0.05 N: Place 2.5 ± 0.2 g Na_2CO_3 (dried at 250°C for 4 hours and cooled in desiccator) into a 1 liter volumetric flask and dilute to the mark. Stock must be standardized. To standardize use the following procedure: Using a clean, glass 10 mL pipet, pipet 10 mL of stock into a beaker containing 80 mL of distilled water and titrate with 0.02 N standard sulfuric acid solution (Section 6.2) until a pH of 4.5 has been reached. This must be done 5 times and any outliers must be thrown out. Calculate concentraction by using the alkalinity calculation. This will give you mg/L $CaCO_3$.

6.2 Standard Sulfuric acid, 0.1 N: A commercially prepared, certified solution from Ricca is used.

6.3 Standard Sulfuric acid, 0.02N: Dilute 200.0 mL of 0.10 N standard sulfuric acid solution (Section 6.2) to 1 liter with distilled water. Standardize by titration of 15.0 mL of 0.05 N $NaCO_3$ solution. A commercially prepared solution can also be used.

7.0 PROCEDURE

7.1 Sample size.

7.1.1 Measure sample out by using a 100 mL graduated cylinder. Sample size should be large enough to use at least 2 mL of titrant and small enough to use less than 50 mL of titrant. ALL GLASSWARE MUST BE CLEAN!

7.1.2 Use a sufficiently large volume of titrant (> 20 mL) to obtain good precision while keeping volume low enough to permit sharp end point.

7.1.3 For <1000 mg $CaCO_3$/1 use 0.02 N titrant.

7.1.4 For >1000 mg $CaCO_3$/1 use 0.1 N titrant.

7.2 Titration

7.2.1 Calibrate the pH meter as in SOP-ASM 3231-007.

7.2.2 Place the sample in the beaker with stir bar and place on magnetic stirrer. Rotate the stir bar to create a small vortex in the beaker. Beaker must be insulated from stir plate with a small thin foam pad.

7.2.3 Place the pH probe into the sample and obtain an initial pH.

7.2.4 Titrate standard acid slowly to obtain a pH of 4.5. This endpoint must not exceed a pH of 4.5.

7.2.5 Record the amount of standard acid used.

8.0 QUALITY CONTROL

8.1 Method blanks (MB) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. MB consists of deionized (DI) water.

8.2 Standard Matrix Spike (SP) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. Pipette 2-20 mL of $CaCO_3$ stock (Section 6.1) into a 100 mL graduated cylinder and bring to volume with DI water. Titrate as a normal sample.

8.3 Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. Pipette 2 mL of $CaCO_3$ stock (Section 6.2) to 100 mL of sample or whatever dilution of sample that was used to determine the sample alkalinity, ie., sample had to be diluted 1:4 due to high concentration of alkalinity, then SPM would also be diluted 1:4 and then spiked with 2 mL $CaCO_3$ stock.

9.0 CALCUALTIONS

9.1 Alkalinity, mg/L $CaCO_3$ = $\frac{A \times N \times 50{,}000}{\text{mL of sample used}}$

where: A = volume of standard acid, mL

N = Normality of the standard acid

9.2 Phenolphthalein alkalinity - The titration from initial pH to a pH of 8.3 using the total alkalinity procedure. The above calculation is used to determine phenolphthalein alkalinity.

9.3 Carbonate alkalinity - This is present only when the phenolphthalein alkalinity is greater than zero but less than the total alkalinity (Attachment A).

9.4 Hydroxide Alkalinity - This is present only when the phenolphthalein alkalinity is greater than half the total alkalinity (Attachment A).

9.5 Bicarbonate Alkalinity - This is present if the phenolphthalein alkalinity is less than the Total alkalinity (Attachment A).

10.0 REFERENCE

Methods for Chemical Analysis of Water and Wastes (EPA 310.1) EPA 60014-79-020, revised March 1983.

11.0 ATTACHMENT

11.1 Attachment A - **ALKALINITIES, AS $CaCO_3$.**

ATTACHMENT A

Alkalinities, as $CaCO_3$

Alkalinity, as $CaCO_3$, mg/L	OH, as $CaCO_3$ mg/L	CO_3, as $CaCO_3$ mg/L	HCO_3, as $CaCO_3$ mg/L
P = O	O	O	T
P < 1/2 T	O	2P	T - 2P
P = 1/2 T	O	2P	O
P > 1/2 T	2P - T	2 (T-P)	O
P = T	T	O	O

Where: P = Phenolphthalein alkalinity

T = Total alkalinity

OH = Hydroxide Alkalinity

CO_3 = Carbonate Alkalinity

HCO_3 = Bicarbonate Alkalinity

Conversion factors from $CaCO_3$ to ionic forms:

OH, as OH^- = OH, as $CaCO_3$ x 0.34

CO_3, as CO_3^{2-} = CO_3, as $CaCO_3$ x 0.6

HCO_3, as HCO_3 = HCO_3, as $CaCO_3$ x 1.22

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: HARDNESS (EPA METHOD 130.2)

Effective Date: 9/28/92

Prepared by: Kathy K. Allen 9/23/92

Reviewed by: Ken U. Erondu Kenneth U. Erondu 9/23/92

Approved by: John J. Mousa John J Mousa 9/28/92
(Gainesville Laboratory Director)

TABLE OF CONTENTS

TITLE: HARDNESS (EPA METHOD 130.2)

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a consistent method for the determination of hardness as $CaCO_3$ in water samples.

2.0 SCOPE

2.1 This method is applicable to drinking, surface and saline waters, domestic and industrial wastes.

2.2 Automated titration may be used.

2.3 The detection limit for this method is 1.0 mg $CaCO_3$/L.

3.0 SUMMARY OF METHOD

The addition of an EDTA titrant to a solution containing calcium and magnesium ions in the presence of a dye (such as Eriochrome Black T) will cause the solution to change from red to blue upon complete complexation of the ions. The volume of titration solution required for complete complexation is converted to mg $CaCO_3$/L through an equation.

4.0 METHOD INTERFERENCES

4.1 Some metal ions may cause an indistinct endpoint. Complexometrically neutral magnesium salt of EDTA is added to the buffer to insure a satisfactory endpoint.

4.2 Suspended or colloidal organic matter may interfere with the endpoint.

4.3 A pH of 10.0 may be conducive to $CaCO_3$ precipitation which will give erroneously low values. Completion of the titration within 5 minutes is recommended.

5.0 APPARATUS AND MATERIALS

5.1 Micro buret and a macro buret.

5.2 Magnetic stirrer and stir bar.

5.3 150 mL beaker.

5.4 50 mL graduated cylinder.

6.0 REAGENTS

6.1 Buffer:

6.1.1 When available, use a commercially manufactured odorless buffer which contains magnesium salt of EDTA, or

6.1.2 Dissolve 16.9 g ammonium chloride (NH_4Cl) in 143 ml concentrated ammonium hydroxide (NH_4OH). Add 1.25 g magnesium salt of EDTA and dilute to 250 mL with distilled water. Or,

6.1.3 If magnesium salt of EDTA is unavailable, dissolve 1.179 g of disodium salt of EDTA dihydrate (analytical reagent grade) and 780 mg magnesium sulfate ($MgSO_4 \cdot 7H_20$) or 644 mg magnesium chloride ($MgCl_2 \cdot 6H_20$) in 50 mL distilled water. Add this solution to 16.9 g NH_4Cl and 143 mL concentrated NH_4OH with mixing and dilute to 250 ml with distilled water. Store solution in a plastic container for up to 1 month.

6.2 Eriochrome Black T indicator, powder, available commercially.

6.3 Standard EDTA titrant, 0.01 M, available commercially.

6.4 Standard Calcium solution, available commercially, 1 ml = 1.00 mg $CaCO_3$.

7.0 PROCEDURE

7.1 Bring samples to room temperature.

7.2 Dilute 25 mL of sample with an equal volume of deionized (DI) water in a 150 ml beaker.

7.3 Add 1 to 2 mL of buffer solution (Section 6.1). pH should be 10.0 $\pm$ 0.1 at this point.

7.4 Add a small scoop of dried powder indicator so that solution is colored, but not opaque.

7.5 While stirring continuously, titrate slowly with standard EDTA titrant (Section 6.3) until reddish color disappears. Solution should be blue at the end point.

NOTE: For titration of low hardness samples, use larger initial volume with proportionately larger reagent volumes and titrate with the micro buret.

8.0 QUALITY CONTROL

8.1 Method blanks (MB) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. MB consists of deionized (DI) water.

8.2 Standard Matrix Spike (SP) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. Add 5 ml of Standard Calcium solution (Section 5.4) to 25 mL DI water and dilute to 50 mL with DI water. Follow the same procedure used for the samples.

8.3 Sample Matrix Spike (SPM) and Sample Matrix Spike Duplicate (SPMD) must be analyzed at a frequency of 5% for every analytical batch unless specified differently by a project. To 25 mL of sample, add 5 mL of Standard Calcium solution (Section 5.4) and dilute to 50 mL with DI water. Follow the same procedure used for the samples.

Note: The actual number of QC required is rounded up to the nearest whole number, i.e., 5% = 1 QC for 1-20 samples; 2 QC for 21-40 samples, etc.

9.0 CALCULATION

$$\text{Hardness as mg } CaCO_3/L = \frac{A \times B \times 1000}{C}$$

Where: A = ml titrant used

B = mg $CaCO_3$ equivalent to 1.00 ml EDTA titrant

C = sample volume

10.0 REFERENCES

10.1 Methods for Chemical Analysis of Water and Wastes (EPA 130.2), EPA 600/4-79-020, revised March 1983.

10.2 Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989

Environmental Science & Engineering, Inc.
Gainesville Laboratory
Gainesville, Florida

TITLE: **TOTAL DISSOLVED SOLIDS (EPA METHOD 160.1)**

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TITLE: TOTAL DISSOLVED SOLIDS (EPA METHOD 160.1)

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a consistent method for determination of total dissolved solids.

2.0 SCOPE

2.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

2.2 The practical range for this method is 10 mg/L to 20,000 mg/L.

3.0 SUMMARY OF METHOD

3.1 A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a pre-weighed dish. The filtrate is then dried to a constant weight at 180° C. The increase in the dish weight after drying represents the total dissolved solids.

3.2 The filtrate from the total suspended solids determination may be used for determination of total dissolved solids.

4.0 METHOD INTERFERENCES

4.1 Highly mineralized waters with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing.

4.2 Samples high in bicarbonate require careful and possibly prolonged drying to insure complete conversion of bicarbonate to carbonate.

4.3 Because excessive residue in the dish may form a water-trapping crust, limit the sample aliquot to no more than 200 mg residue.

5.0 APPARATUS AND MATERIALS

5.1 Glass-fiber filter disks without organic binder (Whatman grade 934AH, or equivalent).

5.2 Filtration apparatus with filter holder and suction flasks.

5.3 Suction Flask.

5.4 Evaporating dishes, porcelain, 100 mL volume.

5.5 Drying oven, for operation at 180 ± 2° C.

5.6 Desiccator.

5.7 Analytical balance, capable of weighing to 0.1 mg.

6.0 PROCEDURE

6.1 Preparation of glass-fiber filter disk: Insert disk, with wrinkled side up, into the filtration apparatus. Apply vacuum and the wash disk with three successive 20 mL volumes of deionized water. Continue applying vacuum until all traces of water are removed. Discard washings.

6.2 Preparation of evaporating dish: If volatile solids are to be measured, heat cleaned evaporating dish at 550 ± 2°C for one hour in a muffle furnace. If only total dissolved solids are to be measured, heat a clean dish to 180 ± 2°C for one hour in an oven. Store in desiccator until needed. Weigh immediately before use. Record weight and dish number in the lab notebook.

6.3 Selection of filter and sample sizes: Choose sample volume that will yield between less than 200 mg dried residue. If more than 10 minutes are required to complete filtration, increase filter size or decrease sample volume.

6.4 Assemble the filtration apparatus and apply vacuum. Shake the samples and transfer 100 mL using a 100 mL graduated cylinder.

6.5 Filter the samples through the glass fiber filter, rinse with three 10 mL portions of distilled water and continue to apply vacuum for about 3 minutes. Remove as much water as possible.

6.6 Dry the evaporated sample for at least one hour at 180 ± 2° C and cool in the desiccator. Weigh the Method Blank (MB) first. MB must be within ± 0.5 mg of original weight before samples can be weighed. If the MB is outside criteria, place the samples and MB back in the desiccator, cool and reweigh. If MB does not fall within the criteria, place the samples and MB in the oven and dry overnight. In the event that the MB is still not within criteria, samples should be re-analyzed.

7.0 QUALITY CONTROL

7.1 Method blanks (MB) must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project. MB consists of deionized (DI) water.

7.2 Replicate samples must be analyzed at a frequency of 5% for every analytical batch, unless specified differently by a project.

Note: The actual number of QC required is rounded up to the nearest whole number, i.e., 5% = 1 QC for 1-20 samples; 2 QC for 21-40 samples, etc.

8.0 CALCULATIONS

Calculate the total dissolved solids present in each sample, in mg/L, as follows:

$$mg/L = \frac{(A - B) \times 1000}{C}$$

where : A = weight of dried residue + dish, in mg

B = weight of dish, in mg

C = sample volume, in mL

9.0 REFERENCES

9.1 Methods for Chemical Analysis of Water and Wastes (EPA 160.1), EPA-600/4-79-020, revised March 1983.

9.2 Standard Methods for the Examination of Water and Wastewater, 17th Edition, 1989.